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CONCEPT DEVELOPMENT OF EXCHANGE LIQUID REGENERATION

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Concepts are described for regeneration of the intermediate liquid used for isotope exchange in indirect laser isotope separation processes where the laser operates on a process gas distinct from the feed stream. The specific case of regeneration of an exchange liquid consisting of water, sodium hydroxide, and dimethyl sulfoxide for a process to separate deuterium from hydrogen using laser irradiation of trifluoromethane gas is developed. A water feed stream is converted to steam which rises in a chemical process column where it redeuterates a descending flow of exchange liquid without causing significant changes in its chemical composition.

INTRODUCTION

In laser isotope separation, laser irradiation of a "process gas" causes a chemical change in only those molecules bearing a specific isotope. Often the process gas is chosen distinct from the feed stream in order to achieve a match between its resonant frequencies and those provided by available lasers. In this case there is a need for an intermediate carrier to transfer the desired isotope from the feed stream to the process gas. This carrier is first brought into contact with the process gas where it gives up the desired isotope. Then the depleted carrier is regenerated by contact with the feed stream.

Of interest is the case of separation of isotopes of hydrogen when they occur in a feed stream consisting of water. A laser isotope separation process under consideration uses a CO₂ laser to irradiate trifluoromethane gas and selectively dissociate those molecules containing a specific isotope. Then the dissociation products bearing the desired isotope are easily retrieved by chemical means. In this manner, deuterium or tritium, for example, can be separated from hydrogen for various purposes. To transfer the deuterium or the tritium from the feed stream to the trifluoromethane, an intermediate carrier is needed. A suitable candidate appears to be an "exchange liquid" consisting of a mixture of water, sodium hydroxide, and DMSO (dimethyl sulfoxide).

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In the original concept/1/, the process to regenerate the exchange liquid had three stages:

1. Removal of sodium hydroxide;
2. DMSO recovery, by distillation to remove water;
3. Mixing feed water with the recovered DMSO and sodium hydroxide.

These stages of separation and mixing were estimated to carry high capital and operating costs. By contrast, the new process does not separate the sodium hydroxide or the DMSO from the exchange liquid. Rather, an exchange column is used to set up a counter-current cascade between the exchange liquid and a rising flow of steam originating from the feed water. In particular, for the case of heavy water production (separation of deuterium from hydrogen), the descending liquid strips heavy water molecules out of the rising steam, so that the exchange liquid is regenerated (redeuterated) by the time it reaches the bottom of the column. A second column for DMSO stripping is placed above the exchange column, in which DMSO vapor is returned to the lower column and prevented from escaping into the environment. The depleted water which was originally resident in the exchange liquid is released as steam at the top of the DMSO stripper. Energy recovery is feasible, in which the enthalpy in the reject steam is transferred to the feed water in a boiler/condenser.

PROBLEMS WITH DISTILLATION PROCESS FOR DMSO RECOVERY

The original plans for a laser heavy water process called for recovery of the DMSO by means of distillation/1/. The heat required by the reboiler, estimated as approximately 700 MW thermal, would have cost about \$80/kg of heavy water product. This was the largest single cost item in the entire heavy water process. Attempts to lower the cost of solvent recovery by vapor compression and multiple effect vaporization seemed to indicate that the increased capital costs for these techniques offset their decrease in energy costs/2/. Thus the cost of the distillation process remained high.

The second problem was precipitation of the sodium hydroxide in the distillation column, because of the poor solubility of sodium hydroxide as the water is extracted from the DMSO/3/. Up to 10 tons per hour of sodium hydroxide could have "salted-out" in the reboiler. The conventional approach to this problem is to remove the dissolved solids prior to distillation in an agitated thin film evaporator/4/. The cost of this process could be as high as \$50/kg of heavy water, though with energy recovery between the evaporator and the distillation column, the overall cost would be less.

Upon reflection, it appears that the high cost of the conventional DMSO operation is due to carrying out separations. It is costly to separate the sodium

hydroxide from the DMSO/water mixture. Then it is costly to separate the DMSO from the water.

This process is discussed further in Appendix I.

ANALYSIS OF OBJECTIVES

The high cost of the conventional solvent recovery process is due to performing separations believed to be necessary. However, the objective is not to separate substances, but rather to restore the deuterium content of the exchange liquid/5/. If a way could be found to exchange heavy water molecules (HDO) for light water molecules in the exchange liquid without performing separations, then the costs could be reduced.

OPTIONS FOR EXCHANGE LIQUID REGENERATION

Semi-permeable membranes could, in theory, be used to permit interchange of water molecules, and only water molecules, between a stream of feed water and a stream of exchange liquid, as discussed in Appendix I. The drawbacks to implementation of this approach are the need to develop a tailor-made membrane, and the present-day high cost of membranes.

A second option is an exchange column for mixing of liquid and vapor as discussed in Appendix I. The apparatus would be similar to the lower section of a distillation column fed with "open steam"/5/. To a first approximation, the water content of the descending exchange liquid remains constant, and therefore no sodium hydroxide precipitation can occur. The exchange liquid is redeuterated (regenerated) by contact with the rising feed steam. The DMSO vapor carried off by the reject steam is recovered and returned by a DMSO stripping column, which is identical to the upper section in the conventional distillation apparatus.

ANALYSIS OF TRAY COLUMN APPARATUS

A tray-column apparatus for exchange liquid regeneration is analyzed in terms of chemical engineering/6/. The apparatus is physically the same as a distillation column fed with open steam. The difference is that the bottom section is operated as an exchange column, not as a "stripping section". For the top section, the purpose and method of operation are the same as in conventional distillation. The basic equations for conservation of matter and conservation of energy are written down in Appendix II, along with the basic assumptions that we have made.

The equations governing the redeuteration of the exchange liquid are worked out from the basic equations for our liquid/steam exchange column, and are found to be in the same form as the standard results for exchange columns. This is taken as proof that when we operate a "distillation" column with a sufficient input of open steam, we can indeed make the bottom section behave like an exchange column, as desired.

The upper section is to be operated under conventional conditions for conventional purposes. Thus there is no risk of it not working. The lower section (the exchange column) has been analyzed, and it appears that it would work, provided no unrealistic assumptions have been made.

CALCULATION OF EXAMPLE FOR 50% DMSO

An example of the proposed system has been worked out. Specialized equations are derived in Appendix III and applied to the case of 50% DMSO in the exchange liquid. The tray-by-tray internal conditions are calculated to provide insight into the operation of the apparatus. Energy recovery is described in Appendix IV, and incorporated into the "engineering" example of Appendix V. In the example we estimate the liquid and vapor flows required for a heavy water plant capable of producing 400 MG/a. The energy cost for the DMSO operation (exchange liquid regeneration) is estimated to be an order of magnitude lower with the new process and apparatus than it would have been in the original concept/1/.

CONCLUSIONS

A new process and apparatus has been proposed for exchange liquid regeneration in the trifluoromethane-based laser heavy water process. A theoretical analysis, presented in this report, shows that the concept is viable. Trouble-free operation is expected, along with substantial energy savings.

If the new system is confirmed, it would mean the cost of the DMSO operation would no longer be a threat to the economic viability of the laser heavy water process. In addition, the low cost of the operation permits more flexibility in the overall process. Previously, the optimum for the plant was slanted toward reducing DMSO recovery costs as much as possible. Now, large variations in DMSO concentration are feasible, and other parts of the process can be optimized toward their best performance.

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APPENDIX I

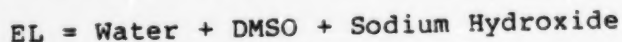
BACKGROUND CONCEPTS

The function of the Exchange Liquid Regenerator (ELR) in a laser heavy water plant is examined, and problems with the conventional apparatus are analyzed.

Concepts for performing the same function without the same problems are developed, starting with selective diffusion through membranes and leading to a liquid/steam exchange column. Ancillary equipment is required to recover DMSO solvent vapor from the reject steam. Energy recovery can be effected through use of vapor compression.

1. The Exchange Liquid Cycle

In Figure 1 we show a schematic diagram of the laser heavy water process based on trifluoromethane. There are three main loops which interact in two exchange regions. If the circulating trifluoromethane could be redeuterated directly by contact with the feed water there would be no need for the intermediate loop. However, to obtain efficient transfer of deuterium, it is necessary to add a catalyst such as sodium hydroxide, and a solvent such as DMSO (dimethyl sulfoxide) to the water. Since the catalyst and solvent must be recovered and recirculated, it is both convenient and instructive to consider an intermediate loop as shown in Figure 1. The fluid circulating in this loop could be called the exchange liquid (EL); and it would consist of sodium hydroxide dissolved in a mixture of water and DMSO. Symbolically we could say:



What happens in the second exchange column is the transfer of deuterium from the exchange liquid to the trifluoromethane gas. Then the exchange liquid needs to be regenerated; that is, its supply of deuterium needs to be replenished. In Figure 1, we show this happening in an apparatus where feed water is brought into contact with the exchange liquid. All that is required for regeneration of the exchange liquid is that the water component be exchanged with the feed stream.

In principle, this could be done through a water-permeable membrane, provided that DMSO and sodium hydroxide were blocked. With counter-current flow as indicated, the concentration of heavy water, HDO, in the emerging flow of exchange liquid would be essentially the same as that of the input stream of feed water, or about 150 ppm. Similarly the deuterium concentration of the reject water would have been lowered to that of the original depleted exchange liquid.

In practice, membranes would not be used because of high cost and the difficulty of tailor-making one for this specific application. However, the membrane analogy will be pursued later as an aid to development of our novel concept.

2. Conventional Exchange Liquid Regeneration

The original concept for handling the DMSO cycle was to recover the DMSO from the depleted water in a distillation column and then the DMSO would be mixed with feed water/1/. The capital cost for this would have been negligible, but the energy cost for distillation would have been the largest single cost item in the entire heavy water plant, about \$80/kg of heavy water produced. This system would have been feasible for the case of a solid catalyst retained in the trifluoromethane exchange column.

However, with dissolved sodium hydroxide as the catalyst, it would have to be removed prior to distillation. This is required because of the poor solubility of sodium hydroxide in DMSO. It has been estimated that several tons of sodium hydroxide could "salt-out" in the reboiler per hour, in the absence of "desalting".

A complete conventional system for regeneration of the exchange liquid is shown in Figure 2. First, the sodium hydroxide is removed in agitated falling film evaporators. One estimate of their capital cost is \$10/kg D_2O . The energy cost could be the order of \$40 per unit of product. The second stage would be distillation to separate the depleted water from the DMSO, so that the water can be discarded. As mentioned above, unit energy costs for this would be about \$80 if energy recovery is not used. Finally, the third stage of the process would be to remix the recovered sodium hydroxide and DMSO with feed water, to thereby regenerate the exchange liquid.

The overall cost of conventional exchange liquid regeneration would be about \$130/kg of heavy water. Even with energy recovery the figure would still be approximately \$100. When the costs of the remaining parts of the process are added in, the economic viability of the original laser heavy water process could be considered marginal.

3. Membrane for Exchange Liquid Regeneration

The role of exchange apparatus in a laser heavy water plant has been discussed above and the principle of operation has been illustrated with membranes. In Figure 3 we use the membrane analogy to progress to the idea of using an exchange column for exchange liquid regeneration. It will be seen that, in an exchange column, the liquid/vapor interface surface acts much like a membrane.

To introduce the topic of exchangers with counter-current flow, consider first a counter-current heat exchanger with equal flows in the two channels. In the ideal case, which could be approached in practice with a long transit time through the apparatus, there would be no temperature gradient in a cross section of the device. That is, portions of fluid adjacent to each other in the two channels would be at the same temperature. This statement would be true, in the ideal case, for fluids at any point in

their travel through the device, including at the ends. Therefore, at each end, the emerging flow will emerge at the same temperature as that of the input flow.

To draw a parallel between heat exchangers and heavy water (HDO) exchangers, it is only necessary to see that heat flow through the septum of a heat exchanger is analogous to the flow of heavy water molecules through the interface surface of an HDO exchanger. Then the intensive variables, temperature, and deuterium concentration, are seen to be analogues.

In Figure 3(a), we show an idealized counter flow exchanger for water molecules. Here, two streams of two different liquids flow through the device in opposite directions. The streams are separated by a semi-permeable membrane, which is assumed to be permeable only to water molecules, H_2O , and HDO. With a sufficiently long transit time (long channels and/or slow flow), an equilibrium would be established across each cross section of the device. As sketched, the cross-flow of water molecules through the interface would be equal from both sides. Given that there were equal longitudinal flows of the two liquids, then the water molecules would have equal concentrations on both sides of the membrane.

The idea is then developed in Figure 3. In Figure 3(b) we let one fluid stream be exchange liquid (EL) and the other be steam, still separated with an ideal membrane. The output exchange liquid would emerge with the same deuterium concentration as that of the input steam. Similarly, the steam would be stripped of deuterium and would emerge at the same depletion level as the depleted input exchange liquid. In Figure 3(c), we introduce a non-ideal membrane which is also somewhat permeable to DMSO. Then the emerging steam would contain some DMSO vapor, which would have to be recovered. The situation is now the same as that in a bubble tray column.

In Figure 3(d), the membrane has been removed; and the interface is the vapor/liquid surface. Each bubble of vapor rising through the liquid in a bubble tray would provide just such an interface. Now, the relative concentration of HDO to H_2O molecules would be the same on each side of the interface (neglecting isotopic relative volatility, a small effect at the temperature envisioned). However, the concentration of DMSO to water molecules would be quite different, as given by the DMSO/water equilibrium curve seen in Figure 11. For example, if half the molecules in the exchange liquid were DMSO, then in the vapor, the fraction of DMSO molecules would be 4%.

Finally, in Figure 3(e), we schematically show recovery and remixing of DMSO.

4. Counter-Current Flow Columns

A counter-current flow column as depicted in Figure 4 with a distillation column could be an economically viable implementation of the ideas developed previously. A column provides a very large contact area in a compact volume. The surface for contact could be the surface of bubbles in a bubble tray, or the wetted surface of the packing in a packed column.

In the HDO exchange section, water molecules, H_2O and HDO, would come into equilibrium in the two counter-current flows: rising vapor and falling liquid. In a packed column with a fine-grained packing, there would be essentially a continuous variation in concentrations through the column, as in the idealized membrane apparatus. If bubble trays were used instead of packing, there would be a distinct variation in concentration from tray to tray. This case will be analyzed below.

What would happen in the exchange section is that heavy water molecules, HDO, would be transferred from the feed steam to the exchange liquid, and thereby it would be redeuterated. There would be no problems with precipitation of sodium hydroxide, since the DMSO would not increase in concentration in the exchange section. The vapor emerging from the top of the exchange section would consist of reject deuterium-depleted steam, a small amount of DMSO vapor, and no sodium hydroxide (since its vapor pressure is zero).

The other part of the apparatus shown in Figure 4 is a specialized distillation column to recover the DMSO from the reject steam. There would be vapor feed to this column. Its upper section could be called a water enriching section or a DMSO stripping section. This section would need to be high enough to meet two objectives: (i) reduce the release of DMSO to the environment to acceptable levels, and (ii) recover sufficient DMSO so that makeup costs would be insignificant. The lower section could be called a water stripping section or a DMSO enriching section. The bottom product from this section would contain the recovered DMSO along with a small amount of deuterium-depleted water. This product could be recirculated by introducing it into the bottom of the exchange section.

5. Concept of Mixing - Tray Column

In Figure 5 we illustrate the concept of mixing as it applies to a tray column. A tray has four parts: two inputs and two outputs, one each for liquid and vapor. If no chemical reactions occur, then all that happens on a tray is that the liquid and vapor inputs are mixed together, and are mixed with the liquid standing on the tray. In a steady state, the total output flow is split into liquid and vapor such that the vapor is in equilibrium with the liquid standing on the tray. In a column, the trays are, in effect, connected in a counter current cascade to provide large separation factors. These principles would apply to both exchange columns and distillation columns. Limiting the present discussion to the water exchange column, we wish to

focus on the process of redeuteration.

In Figure 5(a) we consider mixing equal quantities of water having different deuterium concentrations, say 20 ppm and 150 ppm. The 150 ppm water represents feed water and the 20 ppm water represents the water component of the deuterium-depleted exchange liquid. In batch mixing of equal quantities, then, the deuterium concentration of the product would be the arithmetic average of the two inputs. The same result applies for the tray illustrated in Figure 5(b) provided we assume that the relative volatility of HDO and H₂O is unity. In (c), we show a cascade of two trays. Since the input to one tray is the output from the other, the two are coupled. The system can be solved by solving two equations in two unknowns.

Assuming unity for the relative volatility, then the deuterium concentration is the same in the vapor output from a tray as in its liquid output. Let the upper tray in Figure 5(c) have an output deuterium concentration of x , and the lower one have y . Then the upper tray has inputs of, say, 20 ppm depleted water and y ppm vapor from below. Its output concentration would be the average of the inputs, that is:

$$x = \frac{1}{2} (20 + y).$$

Similarly, the equation for the lower tray is:

$$y = \frac{1}{2} (x + 150),$$

where the vapor input had 150 ppm deuterium.

The solution to these equations is

$$x = 63, y = 107.$$

Thus, the exchange liquid, whose input had water at 20 ppm deuterium, emerges with its water redeutrated to 107 ppm after passing through two trays in cascade.

Clearly, the exchange liquid would be redeutrated to a concentration approaching closer and closer to that of the feed as more and more trays are included in the cascade. Here, we showed the results for one tray and two trays. In the next appendix we treat the general case, with N trays, and obtain general equations for exchange liquid redeuteration in a tray column.

APPENDIX II

ANALYSIS AND PERFORMANCE PREDICTIONS

As shown in Figure 4 we have a system for DMSO recovery consisting of up to three columns. If trays are used, each column, or section, consists of a series of trays connected in cascade, where the outputs of one supply the inputs of adjacent trays. Feed and product are introduced or withdrawn at the interfaces of the columns. Because of the cascading, every tray is ultimately connected to every other tray, and to the feed and product lines. An exact solution to the problem requires that one solve the set of coupled equations describing the complete system. An approximate solution can be obtained by various graphical and analytical techniques.

1. Description of Exchange Liquid

The material being processed is an exchange liquid which consists of four main components of interest:

- light water, H_2O
- heavy water, HDO
- dimethyl sulfoxide (DMSO), $(CH_3)_2SO$
- sodium hydroxide, $NaOH$.

In a bubble rising through the liquid in a tray, these components will come into an equilibrium condition between vapor and liquid.

Above we have explicitly shown the simply deuterated variant of water, HDO , which is the prime carrier of deuterium in the system. Although sodium hydroxide can easily exchange deuterium with water, we do not include deuterated sodium hydroxide in the analysis because its molal concentration will be an order of magnitude lower than that of water. Further, we ignore any deuterium exchange with DMSO, even though it is the most prevalent molecule, because its deuterium exchange rate is believed to be very slow. Thus the DMSO would come to some average value of deuterium concentration, and would then pass around the entire cycle of the exchange liquid with little variation in any one part of the cycle.

Now DMSO is completely miscible in water, and of course heavy water and light water are completely miscible. Thus the composition of tertiary mixture of H_2O , HDO and DMSO can be depicted as a point in a triangle graph for tertiary mixtures, as seen in Figure 6(a). If such a liquid mixture were in contact with a vapor mixture of the same three components, eventually the liquid and vapor would come into equilibrium. Their compositions would be represented by two different points tied together.

At the present time we have no data on the liquid-vapor equilibrium compositions of the tertiary mixture described above. Binary data is available for DMSO and water, as seen in the equilibrium curve shown in Figure 11.

When sodium hydroxide is dissolved in a mixture of DMSO and water, a quaternary solution results with the four principal components listed above. In Figure 6(b) we indicate the approximate equilibrium compositions expected for a "50%" DMSO concentration and 0.1 mol/L of sodium hydroxide.

For the remainder of this analysis we make the following simplifying assumptions:

- (i) Silent Partners. The DMSO and sodium hydroxide are assumed to be silent partners in the HDO exchange column, as far as deuterium transfer is concerned.
- (ii) DMSO vapor pressure not affected by sodium hydroxide. We will use the binary equilibrium data of Figure 11.
- (iii) No isotopic effect in water vapor pressure. The relative volatility of heavy water versus light water is assumed to be unity.

With these assumptions we can begin a preliminary analysis. Additional assumptions will be made as required.

2. Steady-State Rate Equations for One Tray

Each tray, as seen in Figure 7, in a bubble tray column has four "ports". There is a liquid input L_{n+1} coming down from the tray above, or coming in as liquid feed. Similarly, the gas input, G_{n-1} , is forced into the tray from below by a pressure differential. The outputs are a gas stream, G_n , rising from the tray, and a liquid flow, L_n , falling over a weir into the down-comer. In an ideal tray (where the tray efficiency would be 100%), the incoming liquid is thoroughly mixed with that standing on the tray. Also, the gas bubbles have sufficient transit time through the liquid to come into equilibrium with it. Then the output liquid and output gas would have compositions dictated by a point on an equilibrium curve.

In our case, each bubble and its surrounding liquid would be in equilibrium as sketched in Figure 6(b). In Figure 7 we have simplified the drawing by showing only one source of bubbles, whereas in actual practice there would be a large number of openings for the gas flow, to yield a very large bubble surface area.

In a steady-state condition, the tray is full of liquid up to the top of the weir, the flows are steady, and there is no change of composition or temperature. Several equations can be written down to describe the operation of the tray. First consider conservation of material. Every molecule must be accounted for, and since none are building up in the tray in steady state, then molecules leaving must balance those entering. We may conveniently do our molecule counting in terms of moles, which is the number of molecules divided by Avogadro's Number. Letting the flows, L and G , be in units of moles per second, then the total material balance equation is obtained by setting the total output flow equal to the total input flow. Thus we have

$$L_n + G_n = L_{n+1} + G_{n-1} \quad \text{Material Balance,} \quad (1)$$

The individual components of the flows must also balance. Let the mole fraction of molecule i be x_i in the liquid, and y_i in the gas or vapor. Since these are mole fractions, they must add up to unity, that is:

$$\sum_i x_i = 1 \quad \text{and} \quad \sum_i y_i = 1.$$

Then, for molecule i , we have:

$$x_{i,n} L_n + y_{i,n} G_n = x_{i,n+1} L_{n+1} + y_{i,n-1} G_{n-1}$$

$$\text{Component-}i \text{ Balance,} \quad (2)$$

Our four principal components are

- $i = 1$ light water
- $i = 2$ heavy water
- $i = 3$ DMSO
- $i = 4$ sodium hydroxide

Light water balance and DMSO balance would use Equation 2 directly. To simplify matters, we apply the assumptions made in the previous section. The sodium hydroxide has zero vapor pressure, so $y_4 = 0$. As a "silent partner", the sodium hydroxide can be dropped from the analysis, so $x_4 = 0$. When we say the relative volatility of heavy water is unity, we mean

$$\frac{y_2/y_1}{x_2/x_1} = 1$$

Assuming the DMSO and sodium hydroxide are silent partners in deuterium transfer, then the deuterium is carried only by the water component. Let the relative deuterium concentration in the water component be D .

We will generally express D in units of parts per million (ppm). Since we are dealing with small fractions of heavy water, ignore heavy water mol fractions when they are included with light water. Then the deuterium balance condition is

$$D_n x_{1,n} + D_n y_{1,n} G_n = D_{n+1} x_{1,n+1} L_{n+1} + D_{n-1} y_{1,n-1} G_{n-1}$$

Deuterium Balance (3)

where the light water mol fractions are x_1 and y_1 in liquid and gas, respectively. In the special case where all four light water flows were the same, the above would reduce to

$$D_n = \frac{1}{2} (D_{n+1} + D_{n-1}) ,$$

as indicated before in Appendix I, Section 5.

Above, we have considered conservation of matter. Now, let us turn to conservation of energy. Neglecting mechanical energy (kinetic energy of moving fluids, potential energy due to height or pressure) and assuming no chemical reactions occur, we have thermal energy. In a steady state, the temperature of the tray remains constant. Assuming that the column is well insulated, all heat is transported by the flowing fluids. Therefore, the enthalpy (latent heat plus sensible heat) of the output flows must balance that of the input flows. Assuming a simple mixture, then the enthalpy of the mixture is a weighted average of the enthalpies of the components. If component i in isolation has molal latent heat of vaporization λ_i and heat capacity per mol of c_i , then relative to a reference temperature T_r , its enthalpy is $c_i(T - T_r)$ if it is liquid, and $c_i(T - T_r) + \lambda_i$ if it is vaporized. With the above assumptions, then, conservation of energy demands that:

$$\begin{aligned} & L_n \sum_i x_{i,n} c_i (T_n - T_r) + G_n \sum_i y_{i,n} [c_i (T_n - T_r) + \lambda_i] \\ &= L_{n+1} \sum_i x_{i,n+1} c_i (T_{n+1} - T_r) + G_{n-1} \sum_i y_{i,n-1} [c_i (T_{n-1} - T_r) + \lambda_i] \end{aligned}$$

Enthalpy Balance, (4)

Implied above, by not showing any dependence of c_i or λ_i on n , is the approximation that the heat capacity and latent heat do not depend on temperature. (For DMSO, for example, $\lambda_3 = 12.64$ kcal/mol at 25°C, and 10.31 kcal/mol at 189°C.)

The above balance equations have been applied to an individual tray, and show its connections with the adjacent trays. In the following sections we will base an analysis of our various columns on these equations. For the HDO exchange column we will make use of the deuterium balance equation, Equation 3. For the DMSO stripping column, we will need to ensure that the DMSO and water components are balanced, along with enthalpy.

3. Heavy Water Exchange Column

In Figure 8 we show a counter-current flow column in which heavy water is transferred from a flow of feed steam to depleted exchange liquid. On the "silent partner" assumption given above, only the water component of the exchange liquid is significant in

deuterium transfer. With DMSO recirculated to the steam input, as shown in Figure 4, the DMSO concentration would be uniform on all the trays in the HDO exchange column. For steady-state exchange liquid regeneration, the flow of steam will be the same at all trays, including the feed steam input and the depleted steam output. Similarly, the liquid flow will be the same onto each tray. Thus Equation 3 for deuterium balance in the HDO exchange column would become:

$$D_{n+1} = (1+g)D_n - g D_{n-1} , \quad (5)$$

where D_n is the relative deuterium concentration of the liquid on the nth tray. It is also the relative concentration of the vapor rising from the nth tray, since we have assumed a relative volatility of unit.

g is ratio of the water component in the vapor and liquid flows, ($g = y_1 G / x_1 L$), constant for all trays. (This presentation implies that HDO concentrations are small in comparison with H_2O .)

The solution to Equation 5 is:

$$(i) \text{ for } g \neq 1, D_n = g^n A + B , \quad (6)$$

where A and B are constants to be chosen to match the boundary conditions,

$$(ii) \text{ for } g = 1, D_n = n\Delta + D_0 \quad (7)$$

where Δ is the change in deuterium concentration from one tray to the next, D_0 is the input concentration.

Our judgement is that the regeneration process would be most economic when the input steam flow is comparable to the water flow in the exchange liquid. Thus to simplify this analysis we choose $g = 1$. Then the two counter-current flows are equal, as they were in the illustration in Figure 3. However, a more refined analysis of the costs in the overall heavy water process could indicate some benefit from unequal water and steam flows in the HDO exchanger. The isotopic effect in the vapor pressure of water should also be included.

With equal counter-current flows of the water components ($g = 1$), the relative deuterium concentration is given by Equation 7. Since we have assumed unity for the relative volatility of heavy water versus light water, D_n is the concentration of both the liquid and vapor output from the nth tray. As seen in Figure 8, the input feed steam has concentration D_0 , which would be 148 ppm for natural water. The redeuterated exchange liquid would have concentration D_1 , which would be specified by the system designer so that the input to the trifluoromethane exchange column would be sufficiently rich in deuterium. If the HDO exchange column has N trays, then the exchange liquid input concentration would

be designated as D_{N+1} , since this is liquid flow descending to tray N.

From Equation 7 we can see that the per-stage concentration increment can be written as:

$$\Delta = D_1 - D_0 \quad (8)$$

To find the number of trays needed to meet the specified performance, we first write out Equation 7 for D_{N+1} in terms of Δ , and then substitute from Equation 8. Solving this, we find the required number of trays to be:

$$N = \frac{D_1 - D_{N+1}}{D_0 - D_1} \quad (9)$$

where D_1 is for the exchange liquid output, water component

D_{N+1} is for the exchange liquid input, water component

D_0 is for the feed steam

This formula for N is the same as the Kremser-Brown-Souders equation for the case of unity absorption coefficient as found in Reference 6, page 116.

The reject steam has relative deuterium concentration D_N which can be written as:

$$D_N = D_{N+1} - D_1 + D_0 \quad (10)$$

The redeuteration fraction, F, seen in Figure 9, expresses how close the exchange liquid concentration can be brought to that of the feed. In the following we define F and find it in terms of the number of trays N. We write:

$$\begin{aligned} F &= \frac{D_1 - D_{N+1}}{D_0 - D_{N+1}} \\ &= \frac{N}{N+1} \end{aligned} \quad (11)$$

It can be seen that F approaches an asymptote of unity as N becomes large. The "slippage" between F and the asymptote is $1/(N+1)$.

As the HDO exchange column is built higher, the capital costs will increase, and so will the pressure required to move the steam through the trays. Thus, an optimum number of trays would be reached when the benefits of transferring slightly more deuterium to the exchange liquid are offset by the increasing costs (capital and energy for pumping) of the column.

4. DMSO Recovery - Stripping Column

In this section we consider the DMSO stripper shown in Figure 4. Its job is to remove DMSO vapor from the reject steam emerging from the HDO exchange column. This recovers the DMSO for recirculation to the HDO exchange column, and also minimizes environmental contamination. In Figure 10 we show a bubble tray column and define our terms, and indicate the McCabe-Thiele method of analysis/6/.

In this column we are concerned with the change of DMSO concentration as we progress up the column, whereas previously we were concerned with deuterium concentrations in the HDO exchange column. Although these two columns are the same internally, the results are quite different because the boundary conditions (inputs and outputs) are quite different.

The feed to this column would be vapor. There would be no sodium hydroxide contained in the vapor. We will ignore the heavy water component. Therefore, we consider only the two components DMSO and water. Let the water mol fractions be x and y in liquid and vapor, respectively. To construct a McCabe-Thiele diagram we start with the liquid-vapor equilibrium curve for DMSO and water as seen in Figure 11. Next, the operating line is drawn.

We will draw it of slope L/G , and, for simplicity will draw it through the pure water point, rather than the point of intersection of the 45° line and specified distillate concentration. The accuracy will be suitable. Finally, a stair-case construction is drawn between the operating line and the equilibrium curve, starting at the feed end. The points where the stair-case touches the equilibrium line give the compositions on each tray. The other points, where the stair-case touches the operating line, give the component balance as required by Equation 2.

To obtain the McCabe-Thiele construction, we are obliged to make the following assumptions: All liquid flows are the same. $L_{n+1} = L_n \equiv L$. Then from Equation 1 we find that all gas flows are the same. $G_n = G_{n-1} \equiv G$. Therefore, for each tray, there is a constant ratio of liquid to gas flows, $m = L/G$, a constant.

With the above assumptions and definition, Equation 2 becomes

$$x_{n+1} = x_n + \frac{1}{m} (y_n - y_{n-1}) . \quad (12)$$

This gives a prescription to continue construction of the stair-case, once two preceeding trays are known. When continued, it can be seen that the operating line in the McCabe-Thiele method is a straight line of slope m .

The McCabe-Thiele method is a very convenient method to make a rapid assessment of the number of trays needed in a column. We use this approximate method rather than more sophisticated

methods because it is well known that DMSO can be separated from water in such a column. The only system error might be a slight error in the estimate of the number of trays needed. In practice, this error is likely to be less than that due to the uncertainty in the "tray efficiency" used to convert from theoretical trays to actual trays.

However, it should be noted that Equation 4 for enthalpy balance will not be satisfied, in general, when the McCabe-Thiele assumption is made. In our case, the enthalpy per mol of DMSO is relatively close to that of water, so the McCabe-Thiele method should be relatively valid for predicting the composition on each tray.

The water stripper shown in Figure 4 would be of smaller size than the DMSO stripper. Its input would be the liquid output from the bottom tray of the DMSO stripper. This flow would be equal (McCabe-Thiele assumption) to the reflux flow introduced at the top of the DMSO stripper, and would be 10 to 30% of the reject steam flow (for 50% to 75% DMSO in the exchange liquid). Thus the cross sectional area of this column would be relatively small. In addition, few trays would be needed to remove the deuterium depleted water to an acceptable level. In fact, it may be possible to do without the water stripper entirely.

The liquid downflow from the DMSO stripper could be routed directly to the bottom of the H₂O exchange column, especially for the higher reflux ratios required at higher DMSO concentrations. However, it appears that in general, it is sufficient to let the stripper downflow flow directly into the top of the exchanger.

APPENDIX III

EXAMPLE - 50% DMSO

In Figure 4 we show a separate distillation column for DMSO recovery, which may be the preferred arrangement for high DMSO concentrations. On the other hand, for moderate DMSO concentrations it should be possible to dispense with the water stripper, and place the DMSO stripper directly above the H₂O exchange column, as shown in Figure 14. We will attempt to show that this configuration is viable, by finding a solution to the basic equations. This would give us a prediction of the operating point of each tray.

For this example, let us consider exchange liquid with a composition of 50% DMSO, and a low concentration of sodium hydroxide. Let us suppose that the exchange liquid enters the regenerator at 20 ppm deuterium in the water component and that we require it to be brought up to 140 ppm. Suppose that feed steam is available at 150 ppm deuterium. Consider a DMSO recovery specification that the waste water shall have less than 20 ppm DMSO.

1. First Iteration

For simplicity, let us ignore the pressure drop across each tray, so that the entire apparatus is at the same pressure, which we will take to be one atmosphere where data is available. Assume that we have an ideal heat exchanger between the input and output flows of exchange liquid, so that no preheating of the input is needed.

The number of trays needed in the H₂O exchanger is found from Equation 9 as:

$$\begin{aligned} N &= \frac{140 - 20}{150 - 140} \\ &= 12. \end{aligned}$$

These are ideal trays. A somewhat greater number (about 30% more) of actual trays would be needed to obtain the specified performance. The reject steam would have a deuterium concentration from Equation 10 of:

$$D_N = 20 - 140 + 150 = 30 \text{ ppm.}$$

The reject steam contains a certain amount of DMSO vapor. Since this vapor is rising from the feed tray where 50% DMSO liquid is being input, a first approximation would be that the reject steam contains 96% water or 4% DMSO, as obtained from the liquid-vapor equilibrium curve for DMSO and water seen in Figure 11.

By construction of the McCabe-Thiele diagram in Figure 11, it can be shown that the DMSO can be removed to the 200 ppm level with about four trays.

Now consider the top tray of the stripper. It must be supplied with a liquid input or else it would dry up. Such liquid could be feed water. More commonly it is a fraction of the distillate and is referred to as "reflux". The minimum reflux ratio can be obtained from a McCabe-Thiele diagram/6/. We also give it in Equation 21. For this example it is 0.087. The actual reflux ratio to be used would be 10% to 50% greater than this, say about 0.1.

Let us obtain the compositions on the trays on a "per-unit" basis, that is, let the exchange liquid water component have a flow of unity. All this water will be rejected as distillate, so the vapor flow arriving at the top condenser would be 1.1 units per second if the reflux ratio is 0.1. Then, with the McCabe-Thiele assumption, the liquid flow coming down from each tray in the stripper would be 0.1 unit. The composition of this liquid would change, and would become richer in DMSO as it descends. This liquid would then drain down into the top tray of the HDO exchanger, where it would be joined by the input exchange liquid flow as seen in Figure 14.

In the HDO exchange column, then, the liquid flows down from each tray would be the same, under the McCabe-Thiele assumption. (This assumption would be exact if the composition is the same on all trays, since then equal flows would carry equal enthalpies.) With a 50% DMSO exchange liquid, its input flow would be 2 units. This added to the stripper liquid would give a liquid flow in the exchanger of 2.1 units. To a first approximation, the composition of this liquid would be 50% water, and the composition on each tray would be $x = 0.5$. Then, from the equilibrium curve, we would have the composition of the vapor as $y = 0.96$, or 4% DMSO. Then if we specify $g = 1$ in Equation 5 (same flow of water in liquid and vapor), we would find a vapor flow of

$$\begin{aligned} G &= g \times L/y \\ &= 1 \times 0.5 \times 2.1/0.96 \\ &= 1.093 \text{ units.} \end{aligned}$$

Now, at the bottom of the exchanger, we would extract 2 units of liquid as the regenerated exchange liquid, and we would input 1 unit of feed steam (or "open" steam/6/). Therefore, from the above, we see that the extra liquid flowing onto the bottom tray is $2.1 - 2 = 0.1$ units; and the extra vapor rising above it is $1.093 - 1 = 0.093$ units. The fact that these two excess flows do not exactly balance shows the approximate nature of the above calculation.

Although approximate, our first iteration is relatively valid. We can side-step the flow balance problem by saying that the vapor flow is 1.1 units. Then it would be only approximately true to say that the composition on each tray is uniform at 0.5.

To summarize this section, the trays in the HDO exchanger would all have a liquid flow of 2.1 units and a vapor flow of 1.1 units

when the reflux ratio is 0.1. The DMSO concentration would be approximately 0.5 mol fraction on each tray. For 12 theoretical trays, the deuterium concentration would increase by 10 ppm per tray traversed by the exchange liquid. In the DMSO stripper, about four trays would be needed to reduce the emission of DMSO below 200 ppm. A reflux ratio of about 0.1 would be satisfactory.

2. Second Iteration - Interface Equations

Let us start at the bottom tray of the exchange liquid regenerator and work up. We write out the water balance equation, Equation 2, for the bottom tray in Figure 8, and imposing material balance from Equation 1, we find:

$$(L_f + R)x_2 + G_0 = L_f x_1 + (G_0 + R) y_1 .$$

Since we wish to withdraw product at the same composition of DMSO as the feed flow L_f , then we have $x_1 = x_f$, the feed composition. For the special case of steam flow equal to the water component in the exchange liquid, we would have $G_0 = L_f x_f$. For these conditions we find:

$$x_2 = \frac{G_0 + R}{L_f + R} y(x_f) \quad (13)$$

For our example, with $G_0 = 1$, $L_f = 2$

$x_f = 0.5$ and $y(x_f) = 0.96$, we find:

$$x_2 = 0.96 (1 + R)/(2 + R) .$$

Here we have a choice of specifying either x_2 or R .

If we attempt to force a uniform composition, we would set $x_2 = x_1 = 0.5$ in this example. Then we would find $R = 0.087$. As written in the previous section, the minimum reflux ratio is 0.087. Now, this would be expected, since an infinite number of trays are needed to effect a separation if the actual reflux ratio is set equal to the minimum. It would then follow that the composition would be uniform along a finite series of trays.

The only valid solution, then, is to set the reflux ratio to a value greater than its minimum, such as the value $R = 0.1$ we have been using so far in this example. Then $x_2 = 0.503$, a composition with slightly more water than the first tray. As we proceed up the column, we expect the trays to become richer in water. Also, the effect becomes greater with a greater reflux ratio. For $R = 0.2$ instead of 0.1, 52.4% water instead of 50.3%.

The composition of the remaining trays could be found by a continuation of the application of the component balance equation, as used above. Alternatively, a McCabe-Thiele diagram could be constructed. The first point on the equilibrium curve would be

$x_1 = 0.5$, $y_1 = 0.96$. As found above, the first point on the operating line would be $x = x_2 = 0.503$, $y = y_1$. Knowing one point on the operating line, the line may be drawn when we evaluate its slope as $L/G = (2 + R)/(1 + R) = 1.91$, for this example.

An algebraic solution may be found easily if we approximate the equilibrium curve in the region of interest as a straight line. Starting at the bottom tray, the equilibrium curve could be written as:

$$y = y_1 + m_e (x - x_1) \quad (14)$$

where the slope for our example at the point ($x_1 = 0.5$, $y_1 = 0.96$) is $m_e = 0.27$, as read from the equilibrium curve. For water balance, Equation 2 could be written as:

$$x_{n+1} = x_n + (y_n - y_{n-1})/m_o, \text{ for } n > 1,$$

where the McCabe-Thiele operating line has slope $m_o = L/G$. Using Equation 14, and substituting $a = m_e/m_o$, we find

$$x_{n+1} = (1 + a)x_n - a x_{n-1}. \quad (15)$$

This equation has the same form as Equation 5 and its solution has the form given in Equation 6. Thus we have

$$x_n = a^n A + B, \text{ for } a \neq 1.$$

For our example, $m_o = L/G = (2 + R)/(1 + R) = 1.91$. Then $a = m_e/m_o = 0.27/1.91 = 0.14$. To determine A and B, we use the values for x , and x_2 given above. We find then:

$$x_n = a^n \frac{x_1 - x_2}{a(1 - a)} + \frac{ax_1 - x_2}{a - 1} \quad (16)$$

In our example, we can set $a = 0.14$ and obtain the liquid composition of each tray in the HDO exchanger from Equation 16. Then the vapor compositions may be obtained from Equation 14. Doing this, we obtain the compositions shown in Figure 12. For a small value of a , it can be seen that as n increases, x_n rapidly approaches the value given by:

$$x_\infty = B = \frac{x_2 - ax_1}{1 - a} \quad (17)$$

Thus, the trays toward the top of the HDO exchange column will all have essentially the same composition as given by Equation 17. For our example, it would be $B = 0.504$. The corresponding vapor composition would be $y = 0.96 = 0.27(0.504 - 0.5) + 0.961$ as given by Equation 14.

The above derivation of compositions in the HDO exchange column use the McCabe-Thiele assumption that the liquid flow L_n is a constant, L . This is rigorously true only if the molal enthalpy

is independent of composition, or if the composition is constant. In our example, this is essentially the case; and therefore the enthalpy balance condition, Equation 4, will be essentially satisfied for the body of the exchanger. However, the bottom tray is a special case.

For enthalpy balance, the bottom tray would need a heat source, or the input steam would need to be superheated.

Consider $n = 1$ in the enthalpy balance equation, Equation 4, and allow for a heat input Q_1 , since this is an interface tray. Let us consider only the water component (#1, subscripted here as w) and DMSO (#3, subscript d). Let the reference temperature be that of the bottom tray, namely $T_r = T_1$. Note that the input vapor flow, G_0 , is pure steam with $y_1 = 1$. The equation for the bottom tray then becomes:

$$\begin{aligned} & G_1 (y_{w,1} \lambda_w + y_{d,1} \lambda_d) \\ &= L_2 (T_2 - T_1) (x_{w,2} c_w + x_{d,2} c_d) \\ &+ G_0 [c_w (T_0 - T_1) + \lambda_w] + Q_1 \end{aligned} \quad (18)$$

For our example, the "per-unit" flows are $G_0 = 1$, $G^1 = 1 + R$, and $L^1 = 2 + R$, where the reflux ratio $R = 0.1$ in this example. Previously in this section we wrote x for x_w , and used $x_d = 1 - x$, with a corresponding format for vapor composition y . Above, we found $x_1 = 0.5$ and $x_2 = 0.503$ for a reflux ratio of 0.1. Since the second tray has a composition close to that of the bottom tray, the temperature difference $T_2 - T_1$ would be negligible for $R = 0.1$.

Equation 18 would then reduce to:

$$\begin{aligned} & (1 + R) [y_1 \lambda_w + (1 - y_1) \lambda_d] \\ &= c_w (T_0 - T_1) + \lambda_w + Q_1/G_0 \end{aligned}$$

Here, the molal heat of vaporization are $\lambda_w = 9.71$ kcal/mol and $\lambda_d = 11.13$ kcal/mol at $T_1 = 131^\circ\text{C}$. For the example, $y_1 = 0.96$ and $R = 0.1$. The heat capacity of water is 18 cal/mol. With these values, the equation becomes, for $R = 0.1$:

$$Q_1 = [1,050 + 18 (T_1 - T_0)] G_0, \quad (19)$$

where Q_1 is the heat flow in cal/s which must be supplied to the bottom tray of the HDO exchanger (by a heat exchanger)

G_0 is the feed steam flow in mol/s at temperature T_0

T_1 is the temperature in $^\circ\text{C}$ of the bottom tray.

In this section we have assumed zero pressure drops, so that the feed steam would be required at a pressure of one atmosphere. If we supply "saturated" steam, its temperature would be

$T_0 = 100^\circ\text{C}$. Also, at one atmosphere, a 50% DMSO mixture has a bubble point of 131°C . Under these conditions we must supply an extra 1600 cal/mol of feed steam.

Above, we assumed the feed steam would be supplied at "saturation", or at its dew point, and that the extra heat would be supplied by a heater immersed in the liquid in the bottom tray. Alternatively, the heater can be placed in the steam line to superheat it. From Equation 19, no extra heat Q_1 would be required at the bottom tray if the feed steam is raised to $T_0 = 190^\circ\text{C}$.

Thus, heat balance can be ensured for the bottom tray of the HDO exchange column (the tray for steam feed) by a suitable combination of:

- (i) Superheating the steam above its dew point.
- (ii) Supplying heat directly to the bottom tray.

We now have a description of the operation of the HDO exchange column which is mathematically consistent within the framework of the assumptions made. The condition of each tray is shown in Figure 12.

Interface Conditions - Exchanger to Stripper

The DMSO stripper must be interfaced with the HDO exchanger. The liquid inputs to the exchanger top tray are the exchange liquid feed and the liquid down flow from the bottom tray of the stripper. Let the top tray in the exchanger have liquid of composition x_N , the bottom tray of the stripper have x_1' , and the exchange liquid feed have x_f . Then water balance on the top tray of the exchanger (the feed tray) requires that:

$$L_f x_f + R x_1' + G y_{N-1} = (L_f + R) x_N + G y_N,$$

where L_f is the feed flow rate, R is reflux, and the vapor flow is $G = L_f x_f + R$. Now, use of Equations 14 and 16 would lead to the result that, for our example, y_N and y_{N-1} are essentially equal. Thus, water balance occurs if

$$x_1' = [(L_f + R) x_N - L_f x_f] / R. \quad (18)$$

For our example, $L_f = 2$, $R = 0.1$, $x_N = 0.504$, and $x_f = 0.5$, yielding a composition for the bottom tray of the stripper of $x_1' = 0.584$ as shown on Figure 2.

The remainder of the compositions shown in Figure 12 were obtained from the McCabe-Thiele diagram given in Figure 11.

APPENDIX IV

ENERGY RECOVERY

Vapor recompression is an energy recovery technique for distillation columns. In this technique, the vapor emerging at low temperature from the top of the column is compressed until its temperature is high enough to supply the reboiler at the bottom of the column. Thus, the latent heat of vaporization of the top vapor is utilized for boil-up at the bottom, instead of being rejected to the condenser. This technique could be adapted to our exchange liquid regenerator.

In Figure 14, we show a configuration which uses vapor compression for energy recovery. The reject steam from the DMSO stripper is used to boil the incoming feed water in a boiler/condenser. This could be similar in construction to a conventional steam-fed reboiler. The scheme is shown schematically in Figure 13. Here, the feed water at flow rate 1 unit per second is boiled in the boiler/condenser. Heat is supplied by the reject steam which would have a flow rate of $1 + R$ units per second, boiler/condenser. If the feed water is raised to the bubble point prior to the boiler/condenser, then not all of the reject steam would be condensed there, and sufficient trim cooling would be required to condense all of the reject steam. The amount of trim cooling required would be that to condense R units per second of water vapor. Alternatively, the trim cooling could be supplied directly in the boiler/condenser by introducing the feed water at a sufficiently low temperature. An intermediate approach would likely yield the best blend of control capability and economic performance.

After all the reject steam is condensed, it is split into two streams: reflux, and waste water. The ratio of these two flows in the reflux ratio, and would be $R = 0.1$ in the example of Appendix III.

The feed water would all be converted into feed steam in the boiler/condenser. Since any practical heat exchanger, such as this boiler/condenser, has a temperature drop, the feed steam will emerge at a lower temperature and therefore a lower pressure than the reject steam. A compressor is used to raise the pressure of the feed steam to that required at the bottom of the HDO exchange column. For a moderate temperature drop in the boiler/condenser, and for a reasonable pressure drop across each tray, it has been estimated that a single-stage centrifugal compressor may be adequate. The power input into the compressor would appear as a heat flow imparted to the feed steam, so that its temperature would be raised by compression. Thus the feed steam would be somewhat superheated (heated hotter than its "saturation" temperature) by the compressor. To obtain enthalpy balance on the bottom tray would likely require some additional heat input indicated in Figure 13 as trim heating.

We can now compare the energy requirements for exchange liquid regeneration with, and without, vapor compression. Without vapor compression, feed steam would have to be supplied at the pressure seen at the bottom of the column. Let us simplify to the case of zero pressure drops and temperature drops, and consider the 50% DMSO example of Appendix III. Let the latent heat of water be λ . Then the condenser heat load would be $(1 + R) \lambda$ units on a "per-unit" basis. Assuming that the exchange liquid comes in at the same temperature as it leaves, and that the feed water enters at the same temperature as the waste water leaves, then the only heat output from the system would be the condenser heat. Therefore, the input heat requirement would be the same, namely, $Q = (1 + R) \lambda$. This heat would be required at the temperature of the bottom tray, 131°C for 50% DMSO.

With vapor compression, the boiler/condenser would transfer λ units of heat to the feed steam. The amount carried away by the trim condenser would be $R \lambda$ units. By the same argument as above, the heat input required would equal that carried away by the condenser, namely $A' = R \lambda$. Thus the heat needed with vapor compression as a fraction of that needed without it would be

$$\frac{Q'}{Q} = \frac{R}{1 + R} \quad (20)$$

If R is taken as a multiple, C , of the minimum reflux ratio, the above may be written in terms of the minimum reflux ratio $R_{\min}$:

$$R_{\min} = \frac{1 - y_1}{y_1 - x_1} \quad (21)$$

where x_1 is the composition of the liquid on the bottom tray of the DMSO stripping column,

y_1 is the corresponding vapor equilibrium composition.

In our example of the preceeding Appendix, we would have $R_{\min} = 0.087$. We took $C = 1.15$ and used $R = 0.1$ in the example. Then we would find that with vapor compression we would require only 8% as much heat input as without it.

However, going to exchange liquid with 75% DMSO, instead of 50% as used in the example, the minimum reflux ratio would become $(1 - 0.84)/(0.84 - 0.25) = 0.271$. With the same multiplier, C , the actual reflux ratio would be $R = 0.312$, and then Equation 14 would give $Q'/Q = 24\%$. Thus, even at the higher DMSO concentrations, vapor compression would still give significant energy savings.

APPENDIX V

ENGINEERING EXAMPLE

The example of 50% DMSO analyzed in Appendix III is shown in Figure 14 with the incorporation of energy recovery discussed in Appendix IV. The system shown is one in which the liquid downflow from the DMSO stripper is fed onto the top tray of the HDO exchanger. Other configurations are possible, such as return of the stripper downflow to the bottom of the exchanger, or to a DMSO enriching section.

A tray efficiency of 70% was assumed leading to an increase from 12 to 17 trays in the exchanger, and from 4 to 6 in the stripper. The total number of actual trays is then $17 + 6 = 23$ trays. Assuming a pressure drop of 10 cm of water per tray, the column pressure drop would be 0.25 atmosphere, or 190 Torr. The compressor is called on to supply this pressure drop plus that across the boiler/condenser.

A rule of thumb for heat exchangers is that when the trade-off between capital cost and energy loss is made, the temperature drop is often about 10°C . Assuming this temperature drop for the boiler/condenser, the pressure drop between the condenser side and the boiler side would be 234 Torr if the top of the column is pegged at atmospheric pressure.

Thus, the compressor would have an inlet (suction) pressure of 526 Torr, and an outlet pressure of 950 Torr, yielding a required compression ratio of 1.8.

We turn now to sizing. For a 400 Mg/a plant, operating 80% of the time, we would be extracting 12.7 g/s of heavy water from the feed water. This is equivalent to extracting completely all of the heavy water from a feed flow of 86 kg/s. In our example, however, the waste water has 30 ppm heavy water, so the required flow would be 107 kg/s of feed water. For a reflux ratio of $R = 0.1$, and a waste water flow $D = 107$ kg/s, the reflux flow would be 10.7 kg/s, and the vapor flow at the top of the column would be $G = D + R = 118$ kg/s. To avoid flooding, it is estimated that a suitable diameter for the DMSO stripper would be 10 m.

For a 50% mol ratio of DMSO to water in the exchange liquid, it would have a flow rate of $107 \times 78/18 = 454$ kg/s of DMSO. Thus the exchange liquid flow rate would be $107 + 454 = 661$ kg/s. The reflux flow of 10.7 kg/s consists of $10 \times 700/18 = 594$ mol/s. Since the same flow in mol/s emerges from the bottom tray of the stripper with 41.6% DMSO and 58.4% water as seen in Figure 12, this flow is at the mass rate of $594 (0.416 \times 78 + 0.584 \times 18) = 25.6 \times 10^3$ g/s = 25.6 kg/s. Then the total liquid flow down the HDO exchanger would be $661 + 26 = 687$ kg/s. The vapor flow upward in exchanger would be the same as that in the stripper when expressed in mol/s. At the top of the stripper it was 118 kg/s or 6500 mol/s. In the body of the exchanger, the vapor

is 3.9% DMSO as given in Figure 12. Thus the mass flow of the vapor is $6550 (0.04 \times 78 + 0.96 \times 18) = 134 \text{ kg/s}$, in the exchanger. A suitable diameter for the exchanger is estimated as 15 m.

The compressor has a throughput of steam equal to the feed water flow, or 107 kg/s. For this flow rate, a single-stage centrifugal compressor of 77% polytropic efficiency with 5% gear and bearing loss would require a 19.2 MW electric motor of 92%, as given in Table II of Reference 7. (This table is for atmospheric pressure at the inlet.)

Now let us consider an overall energy balance for the system in order to identify heating and cooling requirements. Let the heat exchanger between the feed water and waste water streams have a 10°C temperature drop. Then the feed water enters the boiler/condenser at its bubble point. The entire feed flow (of 107 kg/s) would be vaporized by 107 kg/s of vapor rising from the top of the stripper. The remainder of this vapor (10.7 kg/s for reflux) would be condensed by the trim cooler, which would then have a load of $(10\,700 \text{ g/s}) \times (540 \text{ cal/g}) \times (4.18 \text{ J/cal}) = 24.2 \text{ MW thermal}$. An additional heat loss occurs in the feed water/waste water heat exchanger. With the 10°C temperature drop assumed above, the heat lost is $(10\,700 \text{ g/s}) \times (1 \text{ cal/g}^\circ\text{C}) \times (10^\circ\text{C}) \times (4.18 \text{ J/cal}) = 0.4 \text{ MW thermal}$. Similarly, with the heat lost by the exchange liquid heat exchanger would be as above for the water component plus a contribution for the DMSO component of $(454\,000 \text{ g/s}) \times (0.52 \text{ cal/g}^\circ\text{C}) \times (10^\circ\text{C}) \times (4.18 \text{ J/cal}) = 1.0 \text{ MW thermal}$, for an exchange liquid heat loss of 1.4 MW thermal. Thus the total heat leaving the system would be $24.2 + 0.4 + 1.4 = 26.0 \text{ MW thermal}$.

Now, the electric input to the compressor motor goes partly into heating the motor (8%) and bearings (5%), with the remainder (87%) going into heating the feed steam, for a heat input into the system of $19.2 \times 0.87 = 16.7 \text{ MW thermal}$. Since this is less than the heat lost, the trim heating required is $26.0 - 16.7 = 9.3 \text{ MW thermal}$.

Thus, the energy requirements are estimated to be:

- (i) Electrical - 19 MW
- (ii) Heat - 9 MW at 160°C .

The cost of energy for this exchange liquid regenerator is about 10% of that for the original system described in Reference 1.

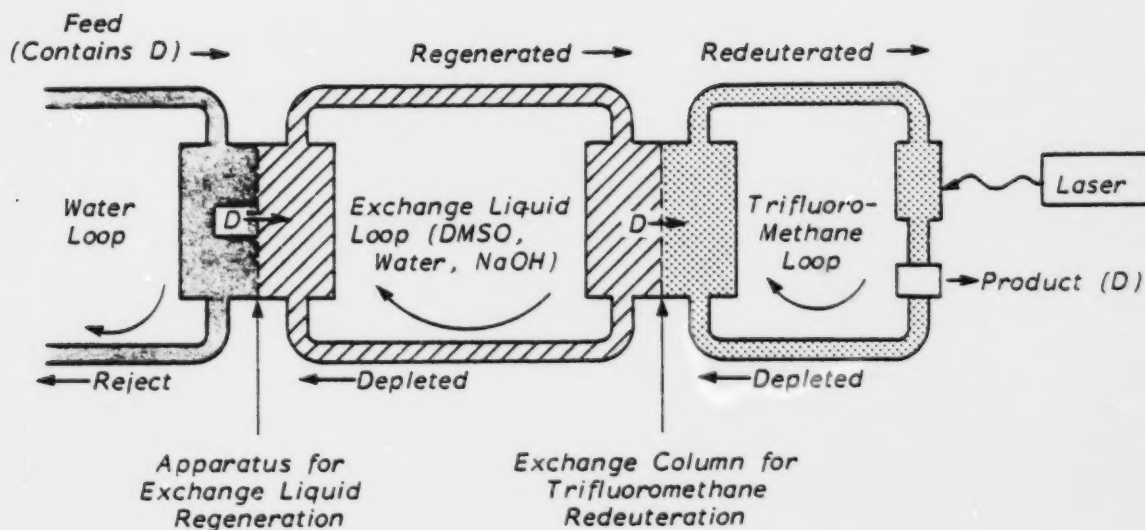


FIGURE 1
THE FRONT END OPERATION IN LASER HEAVY WATER PROCESS

The deuterium D in the feed water is transferred to the exchange liquid, DMSO/water/sodium hydroxide, in an apparatus for exchange liquid regeneration. As sketched, the deuterium could in principle diffuse through a semi-permeable membrane which passes water molecules but blocks DMSO and sodium hydroxide. The exchange liquid would then give up its deuterium to the trifluoromethane process gas in an exchange column. The exchange of deuterium from the water to the trifluoromethane is promoted by the sodium hydroxide NaOH as a catalyst and the DMSO as a solvent. After laser irradiation, a chemical process removes the D-containing photodissociation products.

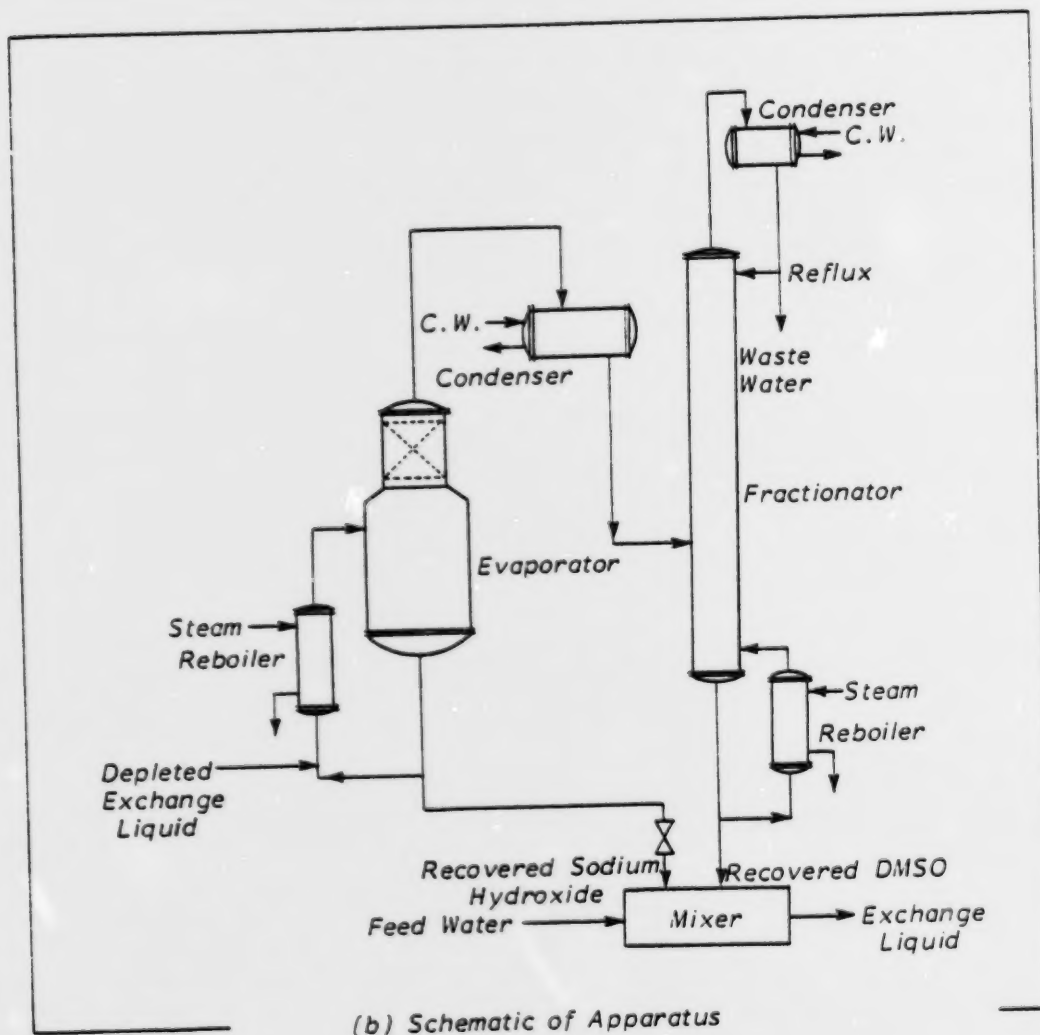
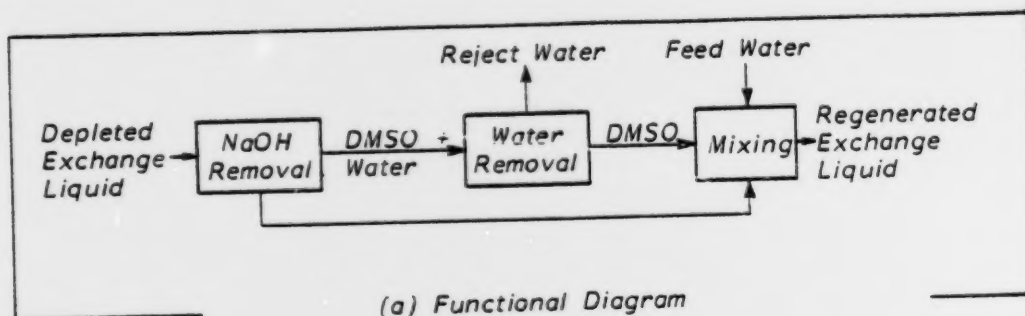


FIGURE 2
CONVENTIONAL EXCHANGE LIQUID REGENERATION PROCESS

The sodium hydroxide would first be removed from the depleted exchange liquid in an agitated thin film evaporator. Then a fractionator (distillation column) would remove the depleted water and would recover the DMSO for remixing with feed water, along with the recovered sodium hydroxide.

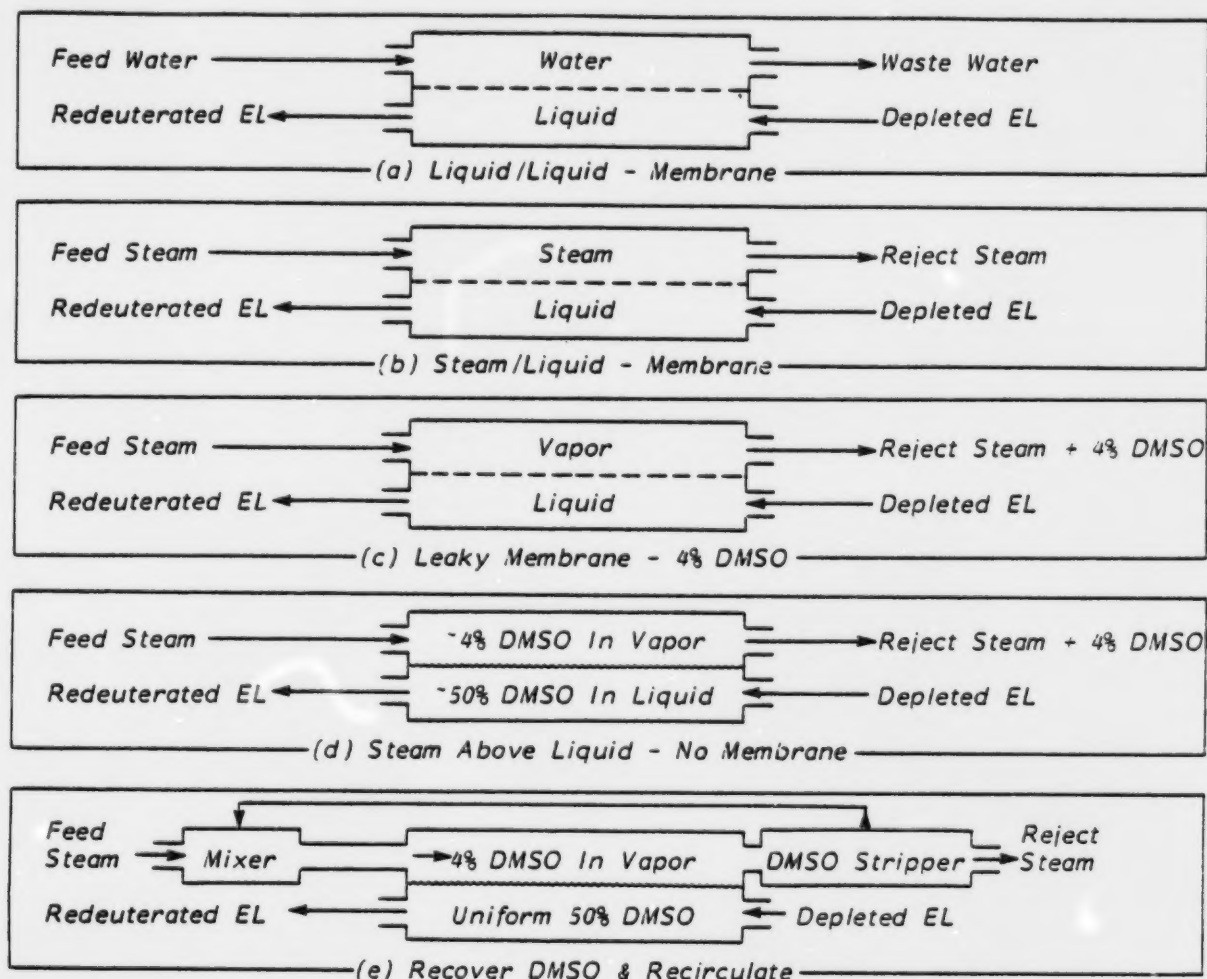


FIGURE 3

EXCHANGE LIQUID REGENERATION BY MEMBRANES, AND VAPOR TO LIQUID EQUILIBRIUM

The exchange liquid (EL) can be regenerated (redeuterated) by arranging for diffusion of water molecules from a feed stream of water or steam. In a) and b) the process can be done with a semi-permeable membrane which blocks the DMSO and sodium hydroxide present in the exchange liquid, but permits water molecules to come into equilibrium, including heavy water. In c) and d), an equivalence is shown between a leaky membrane and the DMSO/water equilibrium concentrations in vapor and liquid. In e) we indicate recovery of DMSO from the reject vapor.

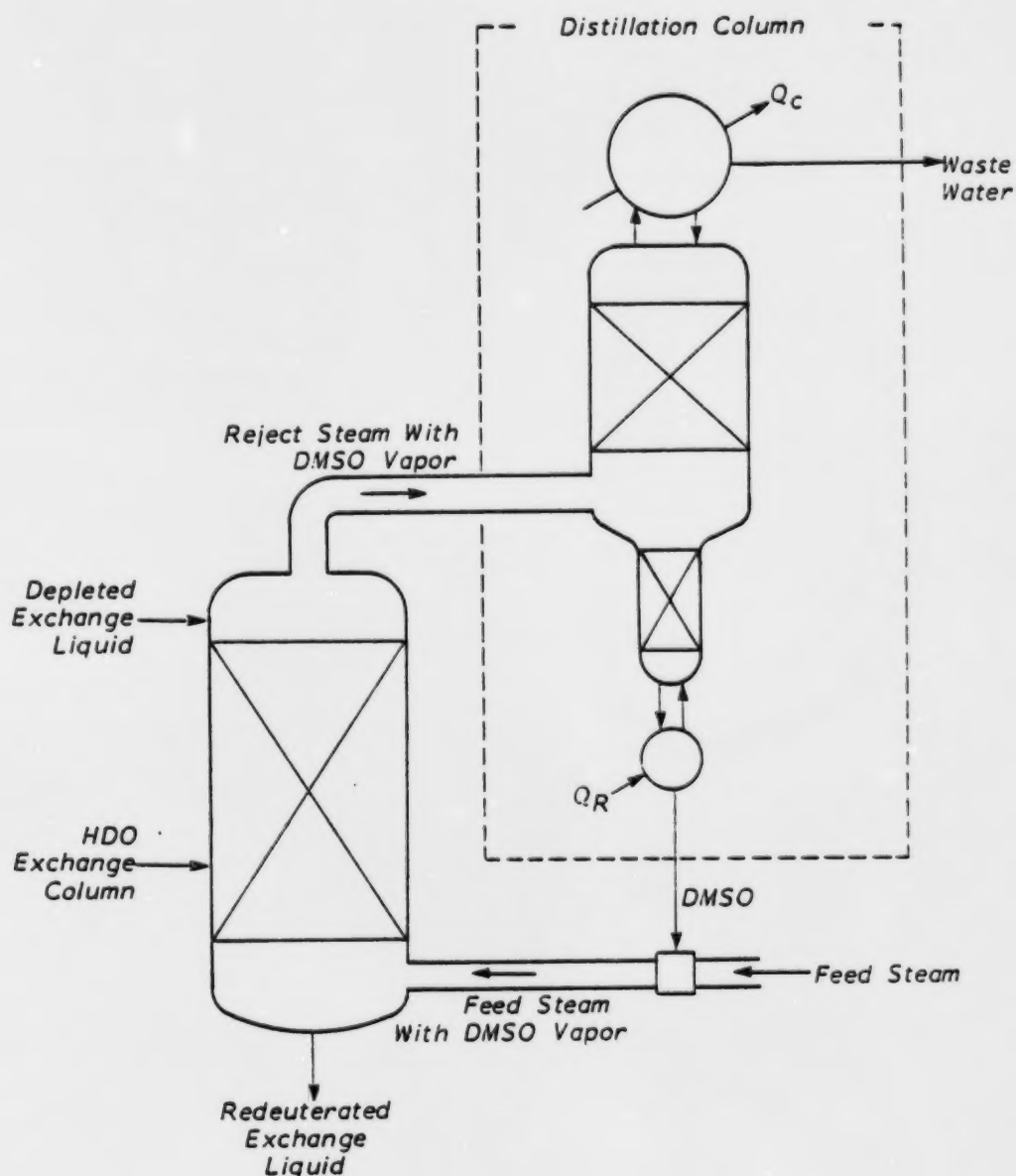


FIGURE 4
EXCHANGE COLUMN FOR EXCHANGE LIQUID REGENERATION

Heavy water molecules HDO can be exchanged efficiently between rising steam and descending liquid in a counter-current flow exchange column. When the feed steam flow is made equal to the flow of the water component in the exchange liquid, the deuterium concentration varies linearly with distance through the HDO exchange column. The distillation column would recover the DMSO from the reject steam and return it to the feed steam line. In this way the rising vapor in the HDO exchange column would always have a constant DMSO to water ratio, and so would the descending liquid. The sodium hydroxide in the exchange liquid would remain entirely in solution; and none of it would be carried into the distillation column.

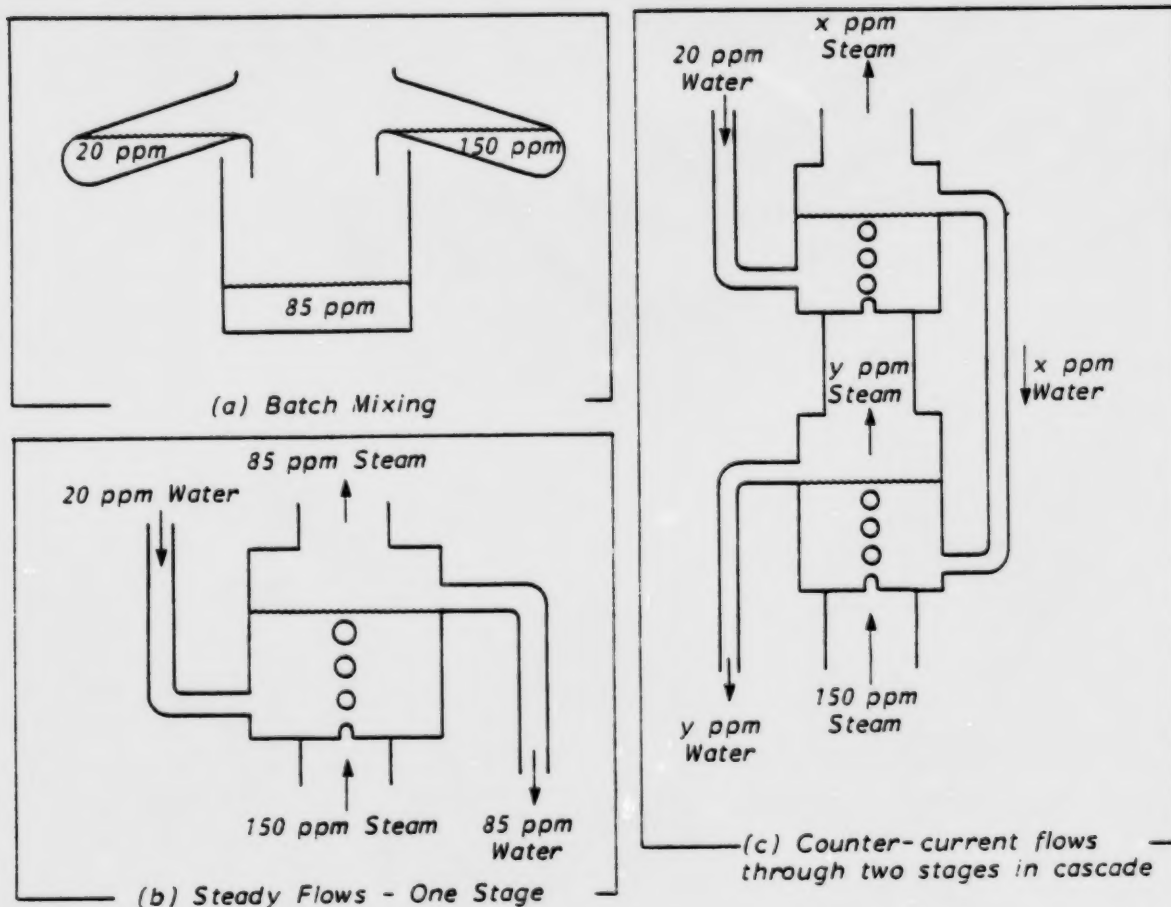


FIGURE 5
ILLUSTRATION OF MIXING IN TRAY COLUMN

In the absence of chemical reactions, mixing is the only phenomenon to occur in a tray. In a) it is seen that the composition of a mixture is the weighted average of the components. In b) the liquid flow represents the water component of the exchange liquid. With an equal flow of steam into the tray, the output liquid and steam would have a deuterium concentration midway between that of the inputs. In c), the concentrations of the outputs of the cascade, x and y , can be found by solving the two coupled equations for the two trays. We find the exchange liquid would be redeuterated to $y=107$ ppm if it had originally been depleted to 20 ppm, and if the feed steam had 150 ppm deuterium. The reject steam would be depleted to 63 ppm.

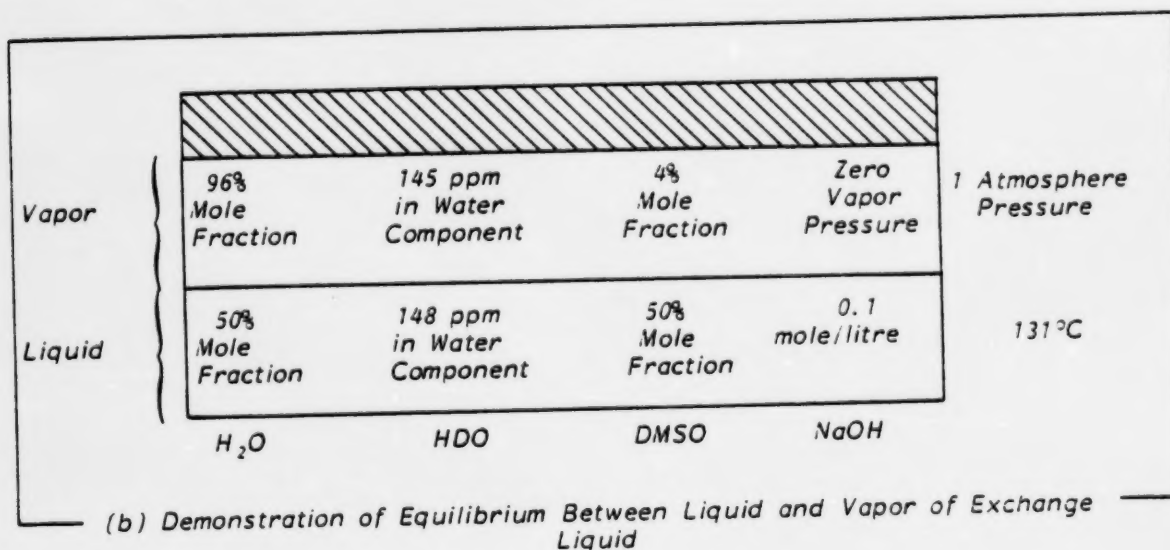
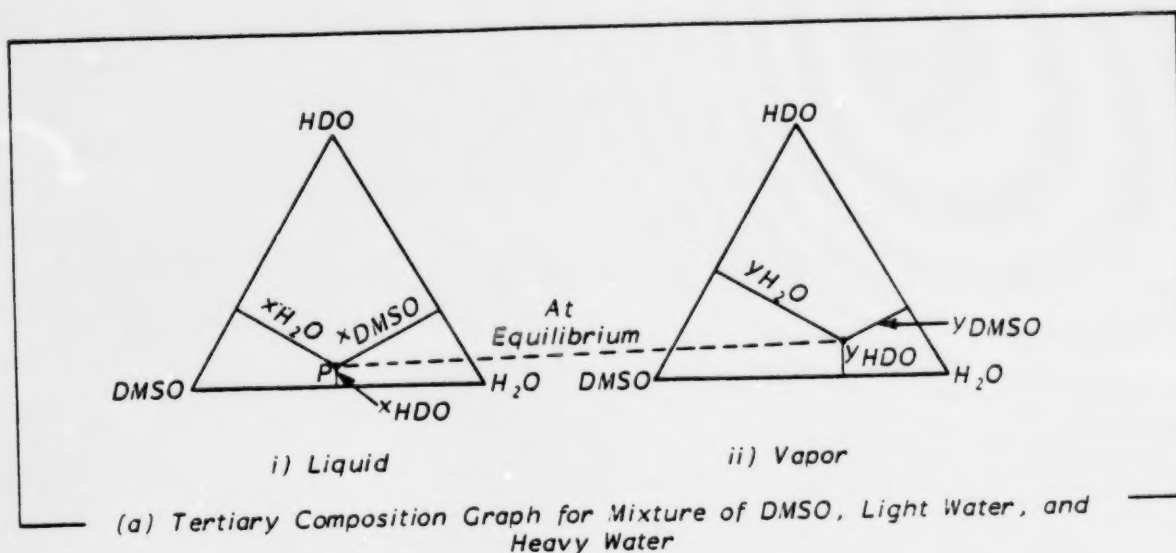


FIGURE 6
DESCRIPTION OF EXCHANGE LIQUID AND EQUILIBRIUM

The components of principal interest in the exchange liquid are: light water H₂O, heavy water HDO, dimethyl sulfoxide DMSO as solvent, and sodium hydroxide NaOH as catalyst. In a) we ignore the sodium hydroxide and show tertiary composition graphs for the volatile components. A composition is defined by point P; and the mole fractions are read as the perpendicular distance to the opposite side of the equilateral triangle. In b) we consider the equilibrium composition set up between vapor and liquid in a sealed container. The same situation would eventually apply to a bubble of vapor rising through liquid on a bubble tray. The compositions shown for a 50% example are approximations based on binary mixture data.

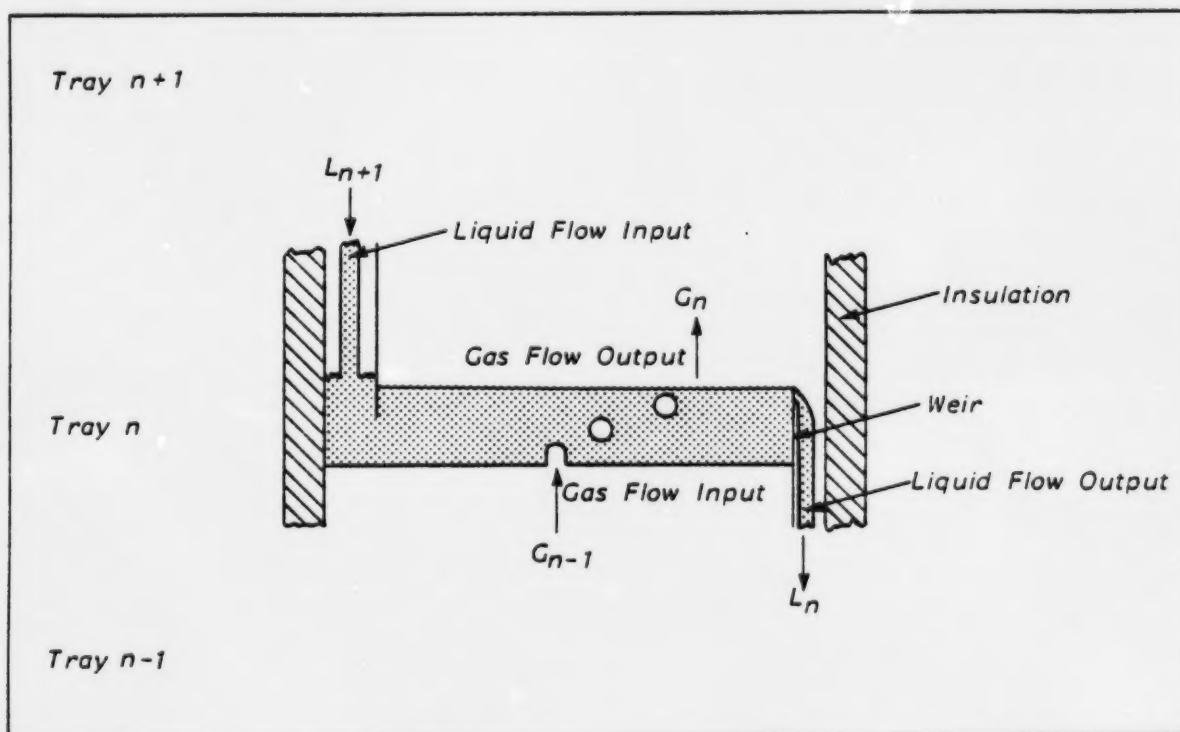


FIGURE 7
DEFINITION OF TERMS FOR SINGLE TRAY

A bubble tray column consists of several trays arranged in a cascade. Each tray has two inputs and two outputs, with flow rates to be given in moles per second. Here we label the bottom tray as number 1, and then count upwards. Tray n receives a liquid input descending from tray $n+1$ above, and a gas or vapor input rising from tray $n-1$ below. Only one source of bubbles is shown for clarity. The bubbles will exchange molecules back and forth across the liquid-gas interface; and will tend to come into equilibrium with the liquid standing on the tray. Thus, for an ideal tray, the gas output and the liquid output would be in equilibrium with each other.

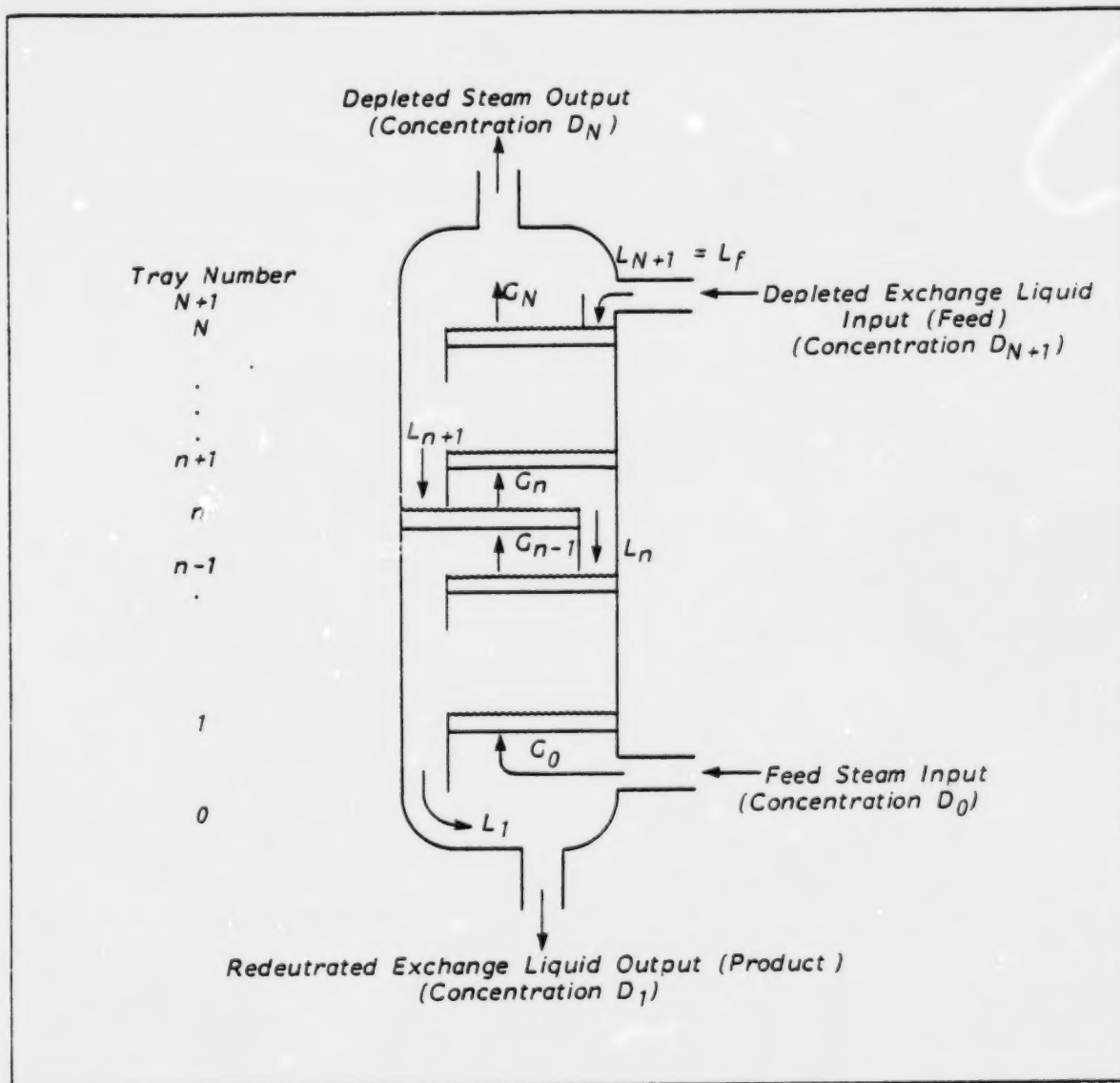


FIGURE 8
TRAY COLUMN FOR LIQUID/STEAM EXCHANGE

A tray numbering scheme is shown for a column operated as an exchange column. With the top tray labelled as N , the liquid feed descending to this tray would appear to originate from tray $N+1$ and is so labelled. Similarly the steam feed at the bottom would appear to originate from one tray below tray 1, and thus is labelled 0. The column's liquid output comes from tray 1, and its vapor output is from tray N . Both the flows, and the deuterium concentrations, are labelled according to their tray of origin.

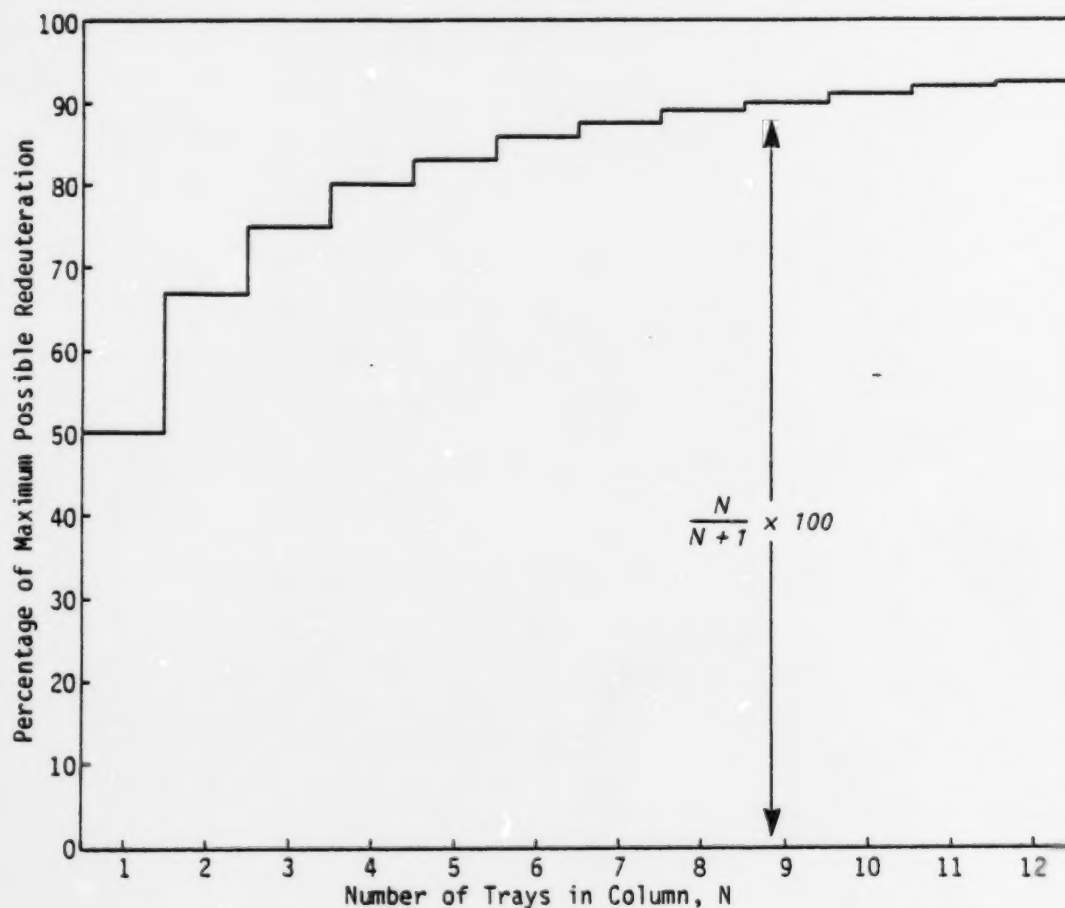


FIGURE 9
REDEUTERATION ACHIEVED IN EXCHANGE COLUMN

Redeuteration of the exchange liquid is improved as the column is made taller, with an asymptotic limit equal to that of the feed steam. The redeuteration fraction is shown for the case where the input steam flow has been made equal to the flow of the water component in the exchange liquid. For N trays, the redeuteration fraction is as shown above; and the slippage from 100% is proportional to $1/(N+1)$.

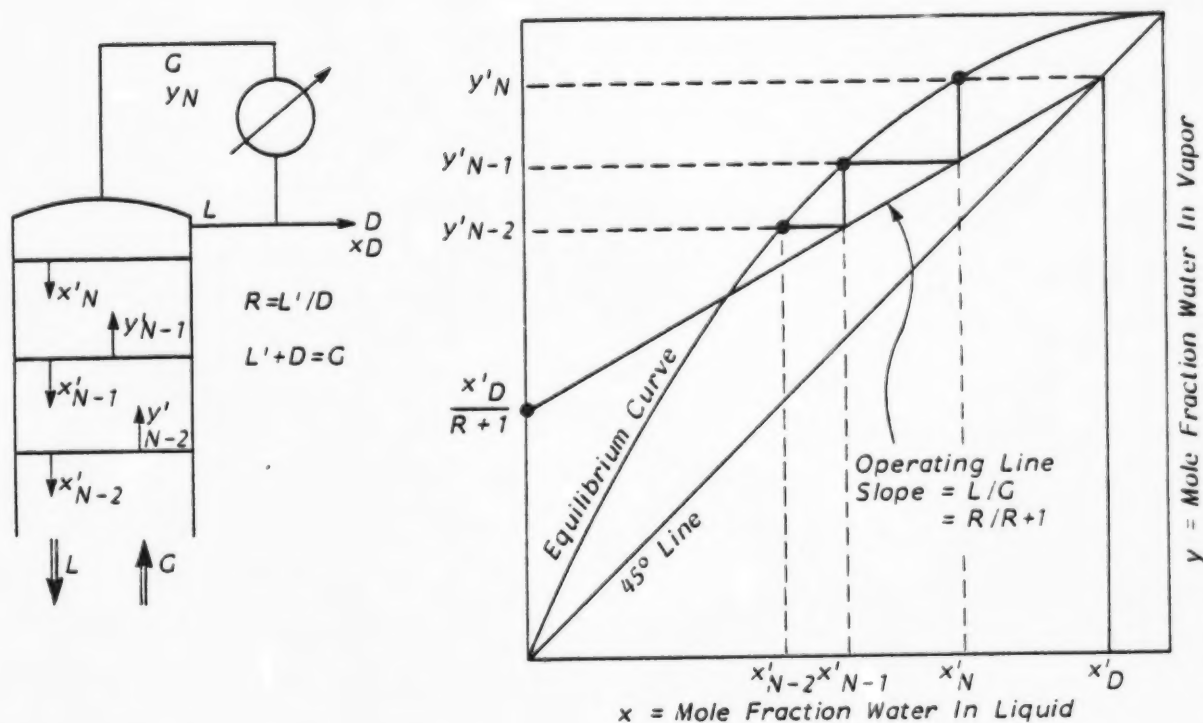


FIGURE 10
DMSO STRIPPING COLUMN AND ANALYSIS METHOD

A tray column operated to strip DMSO out of a DMSO/water mixture can be analyzed by the McCabe-Thiele method. In this method it is assumed that all trays produce the same liquid output L , in moles. Then, for conservation of material, the rising vapor flow will be a constant, G , from each tray. The vapor from the top tray is condensed, and split into two flows: reflux L , and distillate D . In the graphical analysis, the operating line is drawn as indicated on an equilibrium graph, and a stair-case construction is drawn to determine the number of trays required and the composition of each tray's output. The figure is adapted from Figure 9.35 in Treybal/6/.

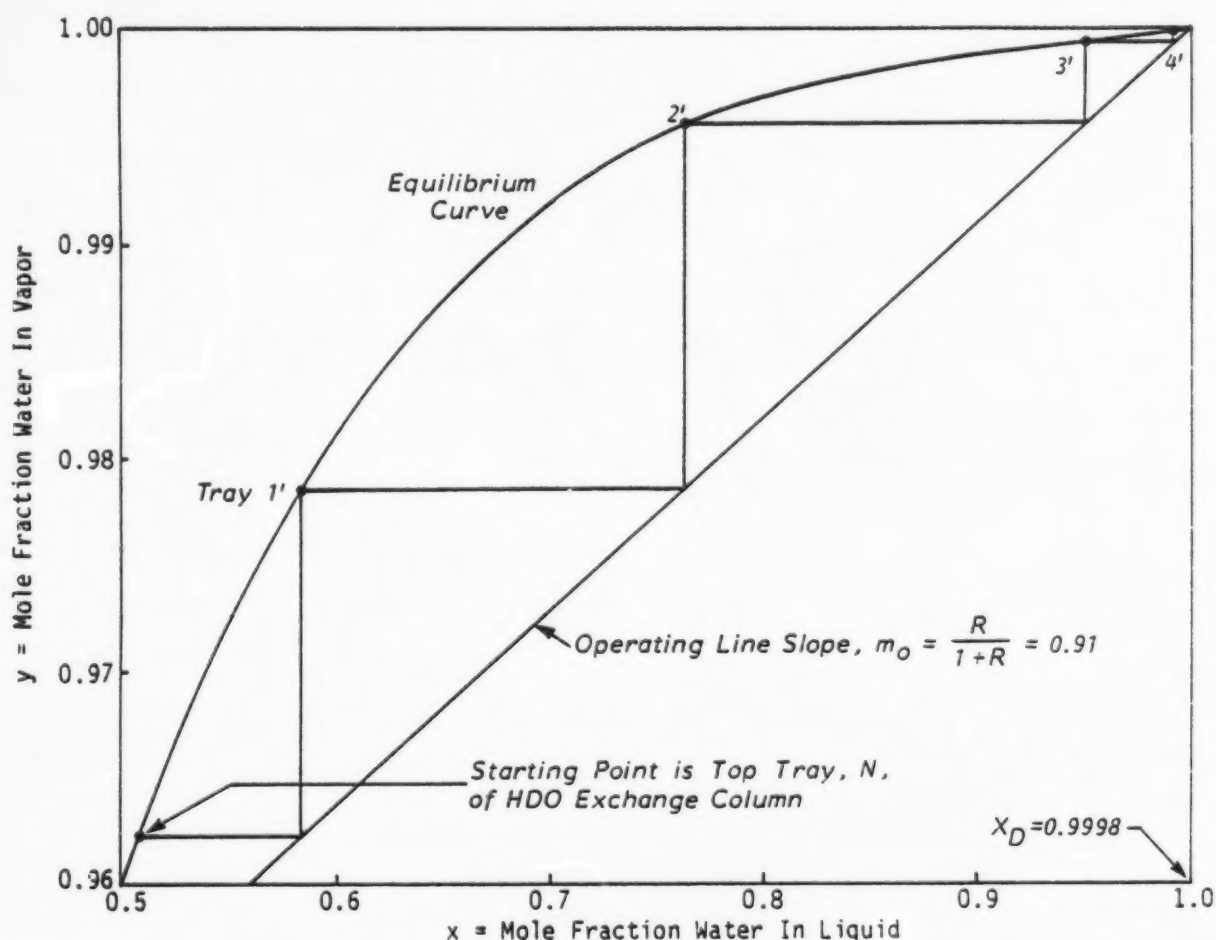


FIGURE 11
McCABE-THIELE DIAGRAM FOR DMSO STRIPPER

This diagram is a blow-up of the region of interest on a McCabe-Thiele drawing for the DMSO stripper in the 50% DMSO example. The distillate D is to be raised to 0.9998 mole fraction water (reduced to 200 ppm DMSO). Assuming an input vapor at 0.96 water, the minimum reflux ratio is 0.087. Here we draw the operating line for an operating reflux ratio of $R=0.1$ and take a distillate concentration of 1 for the first iteration. Our starting point is the top tray, N , of the HDO exchange column. For the 50% case, we found this tray to have composition $x=0.504$, as calculated in the text. Then a staircase is drawn between the equilibrium curve and the operating line until a tray is found with vapor composition less than 200 ppm DMSO. In this example, four theoretical trays would be required.

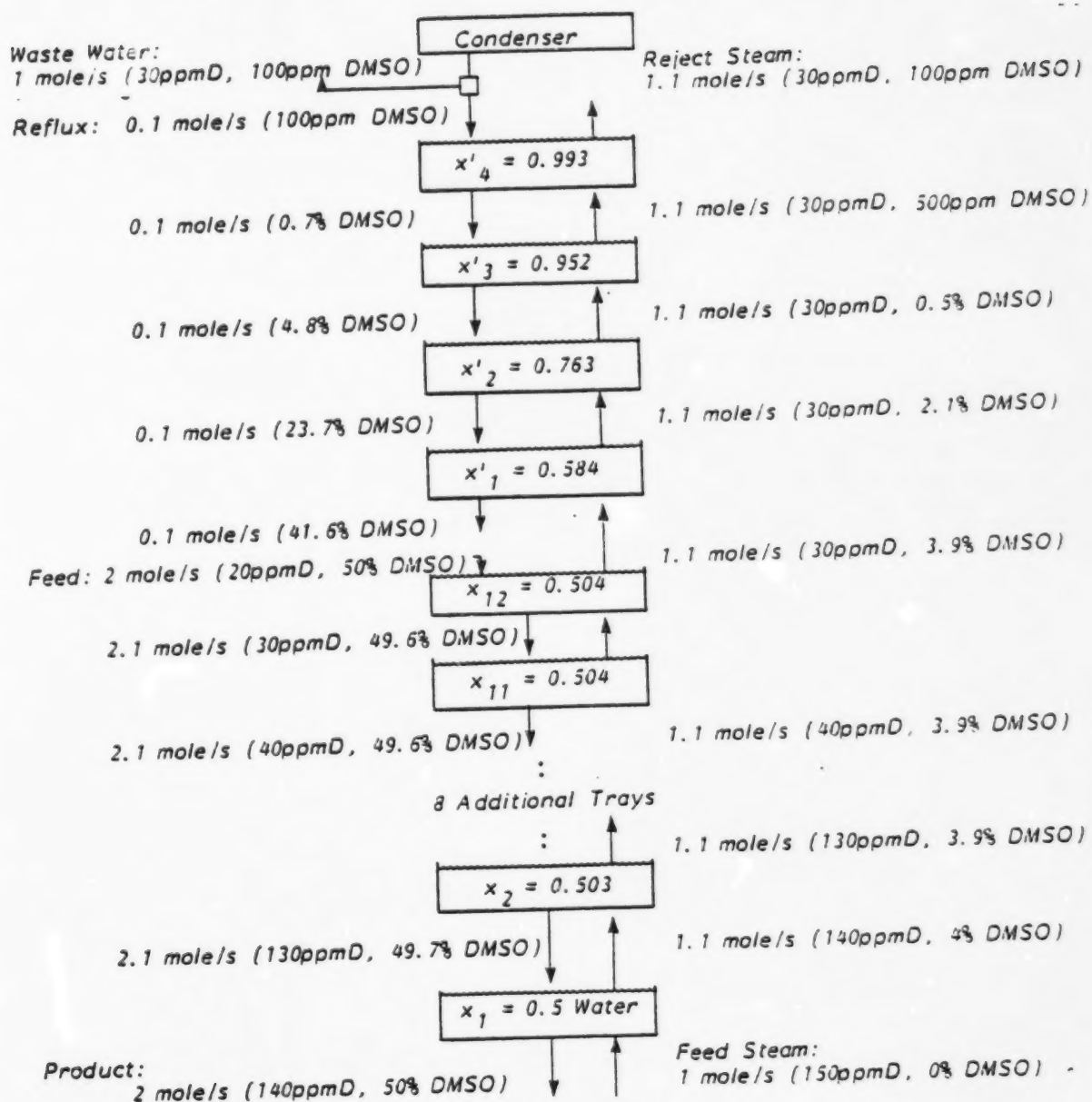


FIGURE 12
TOWER INTERNAL CONDITIONS

An example has been worked out in the text and in the preceding figure for the case of exchange liquid with a DMSO mole fraction of 50%. Here we show the conditions on each tray in both sections of the tower. The lower section is the HDO exchange column, shown with 12 trays. In this column the deuterium concentration in the liquid increases 10 ppm per tray, while the rising vapor loses an equal amount. The DMSO/water composition is seen to be nearly constant in this section. By contrast, conditions are reversed in the top section, the DMSO stripping column. Here, the deuterium concentration is essentially unchanged, while the DMSO composition is reduced to 100 ppm in only four trays. Flows are shown on a "per-unit" basis of one unit per second water in the exchange liquid.

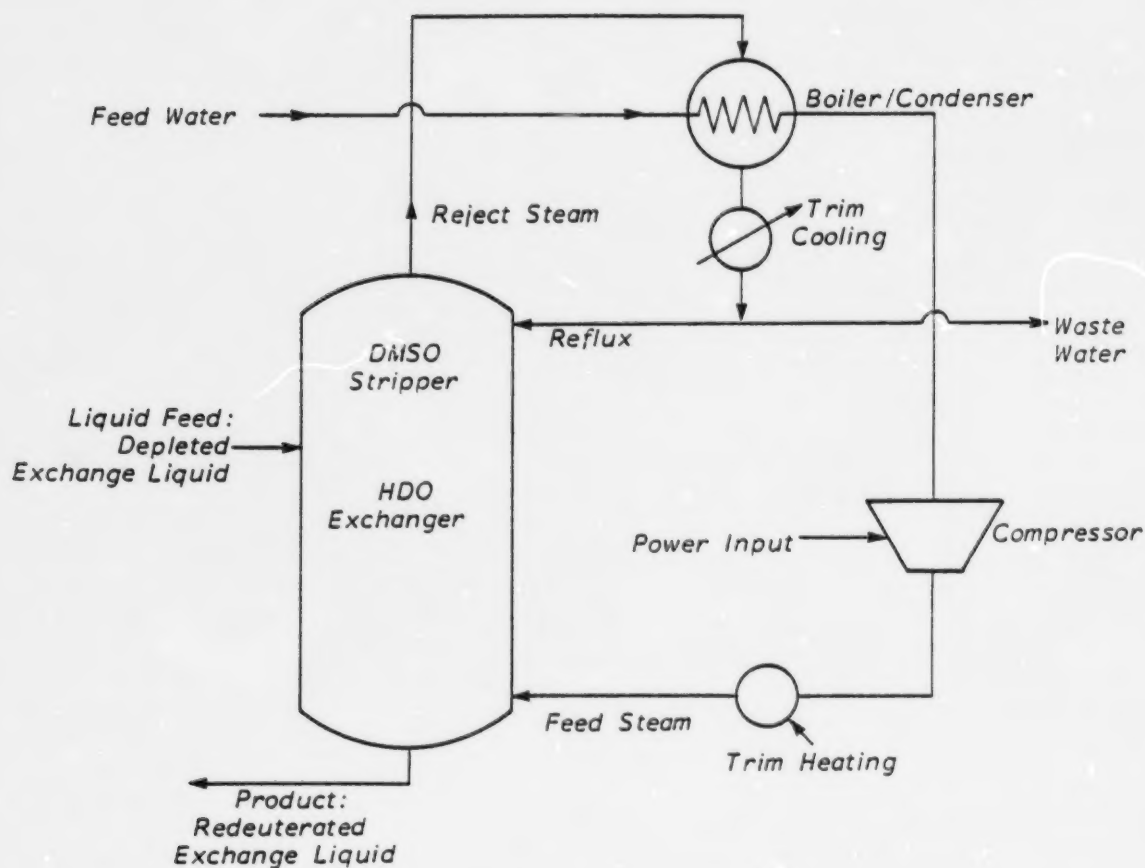


FIGURE 13
ENERGY RECOVERY WITH VAPOR COMPRESSION

Vapor compression could be used for energy recovery in exchange liquid regeneration. In conventional vapor compression, the distillate vapor is first compressed and then used as the heat supply for the reboiler. As shown here, the reject steam is used as heat source to boil the feed water in a boiler/condenser. Then the resultant feed steam is compressed sufficiently to overcome the pressure drop across the tower. Trim heating may be required for enthalpy balance on the bottom tray of the HDO exchanger. Similarly, if there is only partial condensation of the reject steam in the boiler/condenser, then trim cooling would be required.

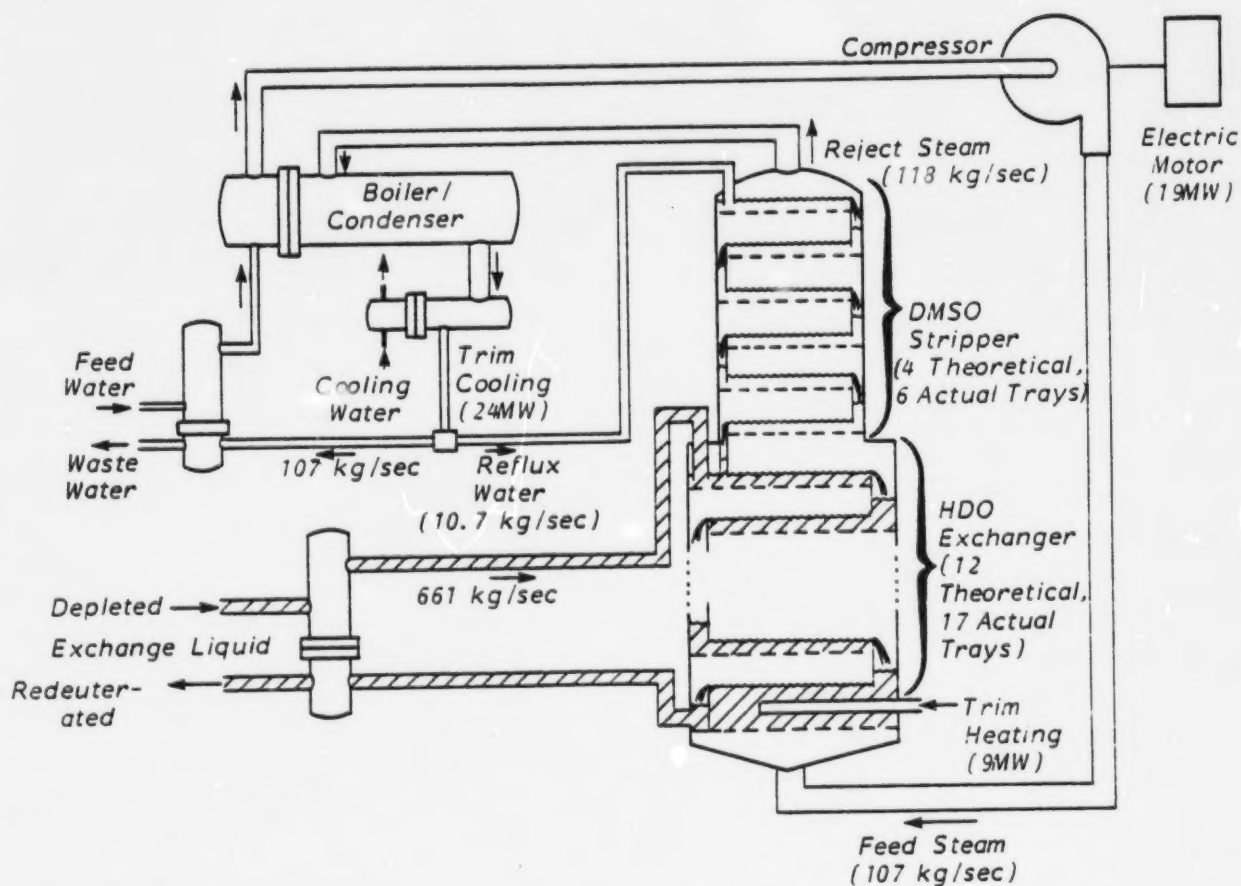


FIGURE 14
APPARATUS FOR EXCHANGE LIQUID REGENERATION

An apparatus for exchange liquid regeneration could be drawn schematically as shown. The tower consists of two sections: an HDO exchanger column and a DMSO stripping column. Bubble cap or sieve trays could be used, as sketched, or a packed column could be used. Various heat exchangers are shown for energy recovery. The principal heat exchanger is a boiler/condenser unit in which feed water is vaporized and most of the reject steam is condensed. A vapor compressor is used to raise the feed steam to a high enough pressure to overcome the pressure drop across the tower and the boiler/condenser. Sufficient trim heating is added to the bottom tray of the HDO exchanger to ensure the required DMSO/water ratio. The numerical values shown are those for the 50% example worked out in the text.